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Article

Preparation of Stable and Metastable Coordination Compounds: Insight into the Structural, Thermodynamic, and Kinetic Aspects of the Formation of Coordination Polymers

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The reaction of ZnI_2 and pyrimidine in acetonitrile results in the formation of the 1:2 compound $ZnI_2(pyrimidine)_2$ (**1**), which consists of discrete tetrahedral building blocks. Slow heating of **1** at 1 °C/min leads to its transformation into the ligand-deficient intermediate 1:1 compound $ZnI_2(pyrimidine)$ (**3**), which upon further heating decomposes into the most ligand-deficient 2:1 compound $(ZnI_2)_2(pyrimidine)$ (**4**). In contrast, the 2:3 compound $(ZnI_2)_2(pyrimidine)_3$ (**2**) is formed as an intermediate by decomposing **1** using a faster heating rate of 8 °C/min. Compound **2** consists of oligomeric units in which each ZnI_2 unit is coordinated by two iodine atoms and one bridging and one terminal pyrimidine ligand. The crystal structure of compound **3** is built up of ZnI_2 units, which are connected by the ligands into chains. For the thermal transformation of **1** into **3** via **2** as the intermediate, a smooth reaction pathway is found in the crystal structure, for which only small translational and rotational changes are needed. The metastable solvated compound $(ZnI_2)(pyrimidine)(acetonitrile)_{0.25}$ (**5**) consisting of $(ZnI_2)_4(pyrimidine)_4$ rings is obtained by quenching the reaction of ZnI_2 and pyrimidine in acetonitrile using an antisolvent. On heating, **5** decomposes into a new polymorphic 1:1 compound **6**, which consists of $(ZnI_2)(pyrimidine)$ chains. On further heating, **6** transforms into a third polymorphic 1:1 compound **7**, which consists of $(ZnI_2)_3(pyrimidine)_3$ rings, and finally into the 1:1 compound **3**. Solvent-mediated conversion experiments reveal that compounds **1**–**4** are thermodynamically stable, whereas compounds **5**–**7** are metastable. Time-dependent crystallization experiments unambiguously show that compound **7** is formed by kinetic control and transforms within minutes into compound **6**, which finally transforms into **3**. Compound **3** represents the thermodynamically most stable 1:1 modification, whereas compounds **6** and **7** are metastable. The different compounds obtained by thermal decomposition and by crystallization from solution represent a snapshot of the species in solution and thus provide insight into the formation of coordination compounds.

Introduction

Recently, the preparation of new coordination polymers, inorganic−organic hybrid compounds, or metal−organic frameworks has become of increasing interest.[1-12] One major goal in this field is the preparation of compounds with desired physical properties, for which structure−property relationships must be investigated and general strategies for a more directed design of solids must be developed.[13-19] However, for any characterization or application, pure compounds are

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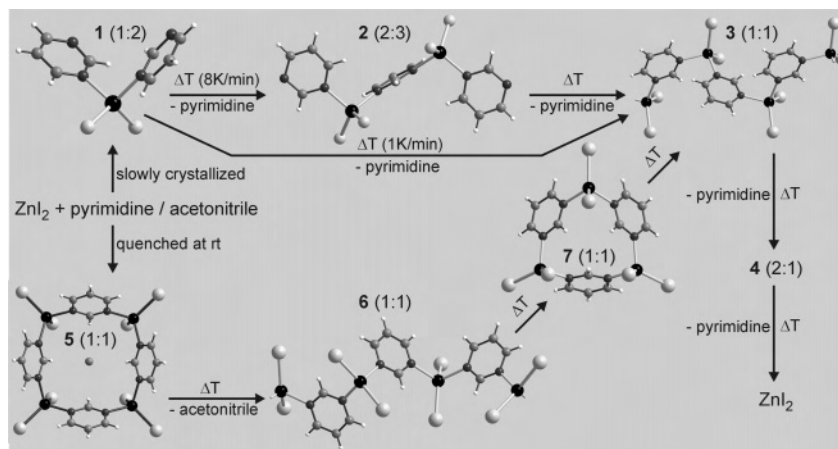(15) Chen, C.-T.; Suslik, K. S. *Coord. Chem. Rev.* **1993**, *128*, 293.

Figure 1. Schematic representation of the thermal decomposition and solution reactions of the different ZnI_2(pyrimidine) coordination compounds reported in this paper.

required in large amounts, and in most cases, syntheses are performed in solution. In solution, different species are in equilibrium, and product formation will depend on a number of parameters like the nature of the solvent, the ratio of the reactants, the stability of the products, etc. In some reactions, metastable compounds can also form in the beginning of the reaction and will transform into the thermodynamically stable compounds as a function of time. In view of this, a mixture of compounds rather than a single product is obtained, or alternatively metastable intermediates might be overlooked. Therefore, alternative preparation methods and investigations on the formation of such compounds in solution are essential.

In our recent work, we have demonstrated that the thermal decomposition of ligand-rich precursor compounds is a convenient method for the discovery and facile synthesis of novel coordination polymers in phase-pure form.[20−27] Starting from ligand-rich precursor compounds, several ligand-deficient intermediate compounds can be obtained during the reaction. By this method, the equillibrium is shifted irreversibly into the direction of the ligand-deficient compounds and, therefore, compounds that cannot be normally prepared in solution or that can only be obtained as mixtures can also be obtained. In addition, by this procedure most compounds that exist in solution can be discovered in a single thermal investigation starting from the most ligand-rich compound. Therefore, such investigations can give information on the species present in solution and the formation of coordination compounds. Here we report on a combined study in the solid

state as well as in solution on a simple system based on ZnI_2 coordination compounds with pyrimidine, which can act as a model for more complex reactions. In these investigations, we have prepared seven different stable and metastable species by thermal decomposition and solution reactions (Figure 1), which were structurally characterized by single-crystal structural analysis and investigated for their kinetic and thermodynamic stability. The results of our study provide insight into the complexity of even simple reactions and into the mechanistic aspects of the formation of coordination polymers.

Experimental Section

Compound 1. ZnI_2 (319.18 mg, 1.0 mmol) and pyrimidine (160.16 mg, 2.0 mmol) were stirred in 0.5 mL of acetonitrile for 1 day at room temperature. Afterward, the precipitate was filtered off. CHN analysis (in %). Found: C, 20.02; H, 1.65; N, 11.44. Calcd for $C_8H_8I_2N_4Zn$: C, 20.05; H, 1.68; N, 11.69. IR (KBr, cm^{-1}): 3049 (w), 2353 (w), 1648 (w), 1589 (s), 1560 (s), 1470 (s), 1373 (m), 1225 (m), 1174 (m), 1081 (m), 1013 (m), 824 (m), 712 (m), 687 (m), 642 (m). Single crystals were prepared by the reaction of ZnI_2 (79.79 mg, 0.25 mmol) with pyrimidine (120.12 mg, 1.5 mmol) at room temperature in 2.0 mL of acetonitrile. Upon evaporation of the solvent, crystals of **1** grew within 7 days.

Compound 2. ZnI_2 (319.18 mg, 1.0 mmol) and pyrimidine (120.12 mg, 1.5 mmol) were stirred in 0.5 mL of acetonitrile for 1 day at room temperature. Afterward, the precipitate was filtered off. CHN analysis (in %). Found: C, 16.71; H, 1.45; N, 9.69. Calcd for $C_{12}H_{12}I_4N_6Zn_2$: C, 16.40; H, 1.38; N, 9.56. IR (KBr, cm^{-1}): 3427 (w), 3091 (w), 3057 (w), 2363 (w), 2344 (m), 1990 (w), 1961 (w), 1916 (w), 1772 (w), 1734 (w), 1717 (w), 1698 (w), 1681 (w), 1653 (w), 1660 (m), 1593 (s), 1560 (s), 1470 (s), 1418 (s), 1367 (m), 1227 (m), 1175 (m), 1082 (s), 1013 (m), 963 (w), 817 (m), 703 (s), 643 (s). Single crystals of the compound were prepared by the reaction of ZnI_2 (159.59 mg, 0.5 mmol) with pyrimidine (40.04 g, 0.5 mmol) in 2.0 mL of acetonitrile. Upon evaporation of the solvent, crystals of **2** grew within 7 days.

Compound 3. ZnI_2 (319.18 mg, 1.0 mmol) and pyrimidine (80.08 mg, 1.0 mmol) were stirred in 0.5 mL of acetonitrile for 1 day at room temperature. Afterward, the precipitate was filtered off. CHN analysis (in %). Found: C, 12.26; H, 0.98; N, 7.10. Calcd for $C_4H_4I_2N_2Zn$: C, 12.03; H, 1.01; N, 7.02. IR (KBr, cm^{-1}): 3123 (m), 3069 (w), 3050 (m), 3027 (m), 2377 (w), 1990 (w), 1900 (w),

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Table 1. Selected Crystal Data and Details on the Structure Determinations[a]

compd	1	2	3	5	6	7
formula	$C_8H_8I_2N_4Zn$	$C_{12}H_{12}I_4N_6Zn_2$	$C_4H_4I_2N_2Zn$	$C_{4.50}H_{4.75}I_2N_{2.25}Zn$	$C_4H_4I_2N_2Zn$	$C_4H_4I_2N_2Zn$
MW/(g/mol)	479.35	878.62	399.26	409.53	399.26	399.26
cryst syst	monoclinic	monoclinic	monoclinic	tetragonal	monoclinic	orthorhombic
space group	$P2_1/n$	$C2/c$	$P2_1/c$	$P4/m$	$P2_1/c$	$Pnma$
Z	4	4	4	8	8	12
temp/K	170	293	293	293	220	220
a/Å	8.0546(6)	23.5621(13)	7.5576(5)	17.0267(8)	6.5487(13)	13.4555(7)
b/Å	12.7334(8)	8.0398(5)	13.5380(8)	17.0267(8)	14.427(3)	19.0259(13)
c/Å	12.6152(12)	11.7637(6)	9.6246(8)	7.5579(4)	18.990(4)	11.285(7)
β/deg	92.208(10)	98.010(6)	112.310(8)		90.021(6)	
V/Å³	1292.89(18)	2206.7(2)	911.02(11)	2191.10(19)	1794.1(6)	2889.0(18)
d_{calc}/(Mg/m³)	2.463	2.645	2.911	2.483	2.956	2.754
μ/mm	6.650	7.777	9.399	7.820	9.546	8.892
min/max transn	0.3223/0.4166	0.2680/0.3858	0.2129/0.3424	0.2304/0.3772	0.1053/0.4472	0.1037/0.4289
θ_{max}/deg	28.0	28.0	28.0	28.0	28.0	28.0
measd reflns	6375	11059	8716	11244	17487	26815
R_{int}	0.0353	0.0834	0.0707	0.0380	0.0721	0.0738
unique reflns	3085	2572	2130	2584	4326	3576
reflns [$F_o > 4\sigma(F_o)$]	2342	2251	1757	2055	3892	3089
param	137	111	84	92	155	128
R1 [$F_o > 4\sigma(F_o)$]	0.0321	0.0319	0.0318	0.0383	0.0334	0.0317
wR2 (all data)	0.0769	0.0839	0.0808	0.1024	0.0767	0.0790
GOF	0.969	1.041	1.065	1.060	1.016	1.028
res elec/(e/Å³)	0.839/−1.163	1.214/−0.973	1.232/−1.345	1.396/−1.064	1.705/−1.217	1.287/−1.718

[a] All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and were refined isotropically ($U_{eq} = -1.2$) using a riding model with C−H = 0.95 Å for aromatic hydrogen atoms. The data were corrected using a numerical absorption correction ($T_{min} = 0.3223$; $T_{max} = 0.4166$). U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

1803 (w), 1708 (w), 1606 (s), 1471 (s), 1404 (s), 1223 (m), 1188 (m), 1080 (s), 1035 (m), 818 (m), 694 (s), 671 (s). Single crystals of this compound were prepared by the reaction of ZnI$_2$ (159.59 mg, 0.5 mmol) with pyrimidine (20.02 mg, 0.25 mmol) in 2 mL of ethanol and 0.3 mL of water. Upon evaporation of the solvent, crystals of **3** grew within 7 days.

Compound 4. ZnI$_2$ (159.59 mg, 0.5 mmol) and pyrimidine (20.02 mg, 0.25 mmol) were stirred in 1.0 mL of heptane for 1 day at room temperature. Afterward, the precipitate was filtered off. In most cases, the product was not phase-pure and was contaminated with ZnI$_2$. Therefore, for further characterization by CHN and spectroscopic analysis, compound **4** was prepared by a thermal decomposition reaction. CHN analysis (in %). Found: C, 6.59; H, 0.56; N, 3.97. Calcd for C$_4$H$_4$I$_4$N$_2$Zn$_2$: C, 6.69; H, 0.56; N, 3.90. IR (KBr, cm^{-1}): 3105 (w), 3063 (w), 2926 (w), 1606 (s), 1562 (m), 1472 (m), 1410 (s), 1369 (w), 1229 (m), 1179 (m), 1144 (w), 1084 (m), 1032 (m), 815 (w), 695 (s), 673 (s), 645 (w).

Compound 5. ZnI$_2$ (159.59 mg, 0.5 mmol) and pyrimidine (40.04 mg, 0.5 mmol) were reacted in 2.0 mL of acetonitrile at room temperature. To the clear solution was added 2.0 mL of carbon tetrachloride as a precipitant, and the residue formed was filtered off. CHN analysis (in %). Found: C, 12.73; H, 1.21; N, 7.96. Calcd for C$_{4.25}$H$_{4.75}$I$_2$N$_{2.25}$Zn: C, 12.56; H, 1.18; N, 7.74. IR (KBr, cm^{-1}): 3102 (m), 3064 (m), 3031 (m), 2920 (w), 2241 (w), 1606 (s), 1568 (m), 1473 (m), 1411 (s), 1368 (w), 1230 (m), 1186 (m), 1151 (w), 1087 (m), 1034 (m), 988 (w), 961 (w), 820 (m), 781 (m), 701 (s), 672 (s). Single crystals of the compound were prepared by the reaction of ZnI$_2$ (159.59 mg, 0.5 mmol) with pyrimidine (40.04 mg, 0.5 mmol) in 2.0 mL of acetonitrile at room temperature. Upon slow evaporation of the solvent, crystals of **5** grew within 3 days.

Compound 6. ZnI$_2$ (159.59 mg, 0.5 mmol) and pyrimidine (40.04 mg, 0.5 mmol) were reacted in 0.5 mL of acetonitrile at room temperature. To the clear solution was added 2.0 mL of carbon tetrachloride as a precipitant, and the residue was immediately filtered off. This compound was really difficult to obtain because in some cases compounds **3**, **5**, or **7** was formed. CHN analysis (in %). Found: C, 12.12; H, 1.07; N, 7.01. Calcd for C$_4$H$_4$I$_2$N$_2$Zn: C,

12.03; H, 1.01; N, 7.02. Single crystals of this compound were prepared by the reaction of ZnI$_2$ (159.59 mg, 0.5 mmol) with pyrimidine (10.01 mg, 0.125 mmol) in 2.0 mL of acetonitrile and 0.3 mL of water. Upon slow evaporation of the solvent from the clear solution, crystals of **6** grew within 2 days.

Compound 7. ZnI$_2$ (159.59 mg, 0.5 mmol) and pyrimidine (40.04 mg, 0.5 mmol) were reacted in 0.5 mL of acetonitrile at room temperature. To the clear solution was added 2.0 mL of carbon tetrachloride as a precipitant, and after 1 h, the product was filtered off. CHN analysis (in %). Found: C, 12.21; H, 1.09; N, 7.11. Calcd for C$_4$H$_4$I$_2$N$_2$Zn: C, 12.03; H, 1.01; N, 7.02. IR (KBr, cm^{-1}): 3107 (m), 3058 (s), 3021 (m), 2923 (w), 2375 (w), 2001 (w), 1812 (w), 1608 (s), 1563 (m), 1472 (s), 1411 (s), 1236 (m), 1189 (s), 1147 (m), 1087 (s),1035 (m), 817 (m), 702 (s), 671 (s). Single crystals of the compound were prepared by the reaction of ZnI$_2$ (159.59 mg, 0.5 mmol) with pyrimidine (40.04 mg, 0.5 mmol) in 2.0 mL of acetonitrile. Upon slow evaporation of the solvent, crystals grew within 1 day.

Single-Crystal X-ray Diffraction. All data were measured using an IPDS-1 with Mo Kα radiation. Structure solutions were performed with *SHELXS-97*, and structure refinements were done against F^2 using *SHELXL-97*. Numerical absorption corrections were performed with X-RED and X-Shape. The metric parameters of compound **6** with $\beta = 90.021$ (6)° indicate that it crystallizes orthorhombic but it is definitely monoclinic. The crystal investigated for this compound is pseudomerohedral-twinned. Therefore, a twin refinement was performed using the twin matrix −1 0 0 0 1 0 0 0 1, which leads to an BASF parameter of 0.326(1). Details of the structure determinations are given in Table 1.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre [CCDC 656322 (**1**), CCDC 656323 (**2**), CCDC 656324 (**3**), CCDC 656325 (**5**), CCDC 656326 (**6**), and CCDC 656327 (**7**)]. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request.cif.

Powder X-ray Diffraction (PXRD). PXRD diffraction experiments were performed using a STOE STADI P transmission powder
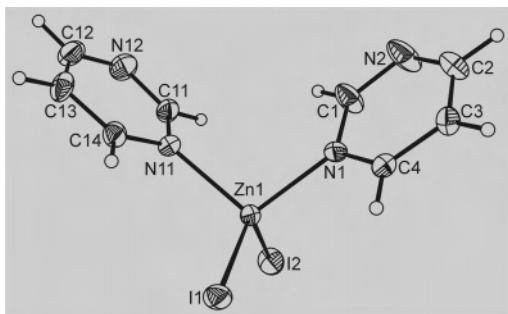
Figure 2. Crystal structure of the ligand-rich 1:2 compound **1** with labeling and displacement ellipsoids drawn at the 50% probability level.

diffractometer with Cu Kα radiation ($\lambda = 154.0598$ pm), which is equipped with a position-sensitive detector (scan range: 5−45°) from STOE & CIE.

Thermogravimetry and Differential Thermoanalysis (TG/DTA). The TG/DTA measurements were performed in a nitrogen atmosphere (purity: 5.0) and Al_2O_3 crucibles using a STA-409CD thermobalance from Netzsch. For the mass spectrometry (MS) measurements, the thermobalance was connected to a quadrupole mass spectrometer from Balzers. All measurements were performed with a flow rate of 75 mL/min and were corrected for buoyancy and current effects. The instrument was calibrated using standard reference materials.

Differential Scanning Calorimetry (DSC). DSC investigations were performed with the DSC 204/1/F device from Netzsch. The measurements were performed in aluminum pans with heating rates of 3 °C/min. The instrument was calibrated using standard reference materials.

Elemental Analysis. CHN analysis was performed using a EURO EA elemental analyzer, fabricated by EURO VECTOR Instruments and Software.

Spectroscopy. Fourier transform IR spectra were recorded on a Genesis series FTIR spectrometer, by ATI Mattson, in KBr pellets.

Results and Discussion

The reaction of ZnI_2 with pyrimidine in acetonitrile leads to the ligand-rich 1:2 compound diiodobis(pyrimidine-*N*)-zinc(II) (**1**), which crystallizes in space group $P2_1/n$ with $Z = 4$ and all atoms in general positions. In this structure, the zinc atoms are coordinated by two iodine atoms and two pyrimidine ligands within distorted tetrahedra into discrete complexes (Figure 2 and Table 2).

TG/DTA measurements on **1** with 1 °C/min in a nitrogen atmosphere show four mass steps, which are accompanied by four endothermic events in the DTA curve, and from the DTG curve, it is obvious that all steps are well resolved (Figure 3). The experimental mass loss of 16.7% in the first TG step is in good agreement with that calculated for the removal of one pyrimidine ligand of 16.7%. The experimental mass losses in the second and third TG steps of 8.3 and 8.5%, respectively, indicate the loss of 0.5 mol of the pyrimidine ligands ($\Delta m_{theo} - {}^1/_2$pyrimidine = 8.35%). The final product after the third step was identified as ZnI_2 by PXRD. On the basis of the above results, it can be inferred that in the first TG step a 1:1 compound of composition ZnI_2-(pyrimidine) (**3**) is formed, whereas the second step leads to the formation of a 2:1 compound of composition $(ZnI_2)_2$-(pyrimidine) (**4**), which upon further heating decomposes into

Table 2. Bond Lengths [Å] and Angles [deg] for Compounds **1**−**3**[a]

Compound **1**			
Zn1−N1	2.070(4)	Zn1−I1	2.5429(7)
Zn1−N11	2.081(4)	Zn1−I2	2.5455(7)
N1−Zn1−I1	106.42(12)	N11−Zn1−I1	106.04(12)
N1−Zn1−I2	109.39(12)	N11−Zn1−I2	106.29(13)
I1−Zn1−I2	123.32(2)	N1−Zn1−N11	103.72(16)
Compound **2**			
Zn1−N11	2.072(4)	Zn1−I2	2.5241(6)
Zn1−N1	2.098(3)	Zn1−I1	2.5539(6)
N11−Zn1−N1	101.76(14)	N11−Zn1−I1	104.77(11)
N11−Zn1−I2	111.29(12)	N1−Zn1−I1	106.03(10)
N1−Zn1−I2	110.43(9)	I2−Zn1−I1	120.75(2)
Compound **3**			
Zn1−N1	2.109(3)	Zn1−I1	2.5245(6)
Zn1−N2A	2.102(3)	Zn1−I2	2.5263(7)
N2A−Zn1−N1	96.37(14)	N2A−Zn1−I2	108.97(10)
N2A−Zn1−I1	110.07(10)	N1−Zn1−I2	107.03(11)
N1−Zn1−I1	107.18(10)	I1−Zn1−I2	123.69(2)

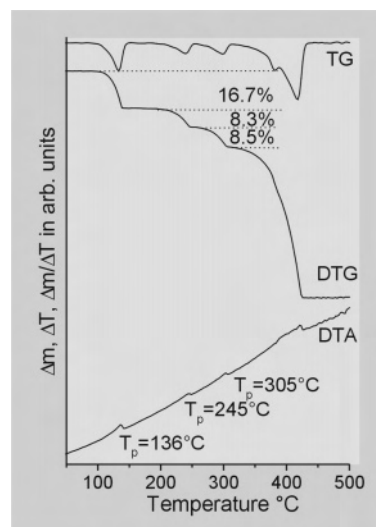[a] Symmetry codes for **3**: A = x, $-y + {}^1/_2$, $z - {}^1/_2$.

Figure 3. DTG, TG, and DTA curves for compound **1** with 1 °C/min.

ZnI_2, which vaporizes in the last TG step. These conclusions are supported by PXRD and elemental analysis of the residues formed in each of the TG steps (see the Experimental Section).

Single crystals of **3** were grown in solution (see the Experimental Section), and crystal structural analysis shows that this compound crystallizes in space group $P2_1/c$ with $Z = 4$ and all atoms in general positions. In diiodo(μ_2-pyrimidine-*N,N'*)zinc(II) (**3**), the zinc atoms are coordinated by two iodine atoms and two pyrimidine ligands within distorted tetrahedra (Figure 4). Most bond lengths and angles are comparable to those in compound **1**, but the Zn−N distances are slightly elongated (Table 2). In contrast to **1**, the ZnI_2 units are connected by the pyrimidine ligands via μ-N,N′ coordination into chains that elongate in the direction of the *a* axis (Figure 8, bottom).

For the ligand-deficient 2:1 compound **4**, no single crystals could be grown and, therefore, this compound was characterized only by PXRD and elemental analysis (see below).
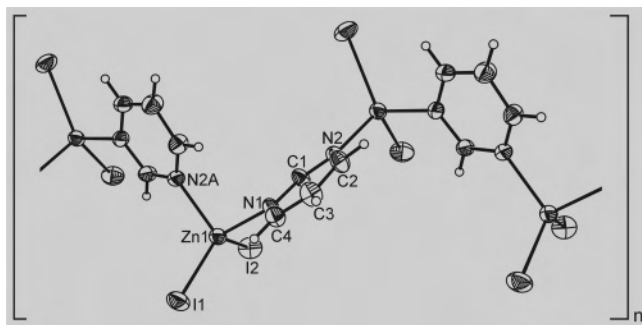
Figure 4. Crystal structure of the 1:1 compound **3** with labeling and displacement ellipsoids drawn at the 50% probability level.
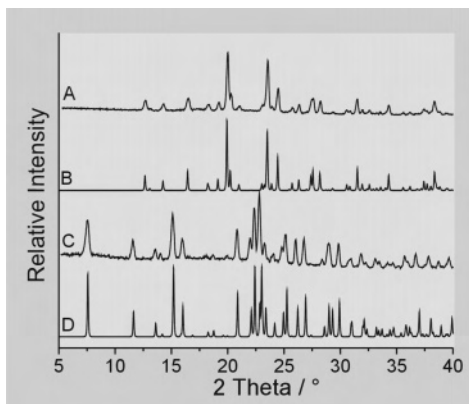

Figure 5. Experimental PXRD patterns of the residue obtained after the first (A) and second (C) TG step in the thermal decomposition reaction of compound **1** and calculated PXRD patterns for the 1:1 compound **3** (B) and the 2:3 compound **2** (D).

Figure 6. Heating rate dependent TG curves for **1** (from left to right: 1, 2, 4, 8, and 16 °C/min).

Figure 7. Crystal structure of the 2:3 compound **2** with labeling and displacement ellipsoids drawn at the 50% probability level.

However, from the composition of this compound, it can be expected that its structure might consist of a more condensed ZnI substructure like, e.g., ZnI_4N_2 octahedra connected via common corners.

To definitely prove the formation of the 1:1 compound **3** in the beginning of the thermal reaction, an additional TG experiment was performed, and the heating was stopped immediately after the first TG step. The residue thus obtained was investigated by PXRD. The experimental powder pattern of this residue is in good agreement with that calculated for compound **3** from single-crystal data, indicating its formation as an intermediate in very pure form (Figure 5). These findings are further supported by elemental analysis (see the Experimental Section).

From investigations reported previously, it is known that in some cases the product formation depends on the kinetics of all reactions involved and, therefore, can be influenced by heating rate dependent measurements.[24] In view of this, the thermal decomposition of the ligand-rich 1:2 compound **1** was investigated using different heating rates. This study revealed that the first mass step is split into two different steps upon faster heating and that the best resolution is obtained with 8 °C/min (Figure 6). The PXRD pattern of the residue formed in the first TG step with 8 °C/min is completely different from that of compounds **1** and **3**, and elemental analysis of this residue is in good agreement with that calculated for a 2:3 compound of composition $(ZnI_2)_2$-(pyrimidine)$_3$ (**2**; see the Experimental Section).
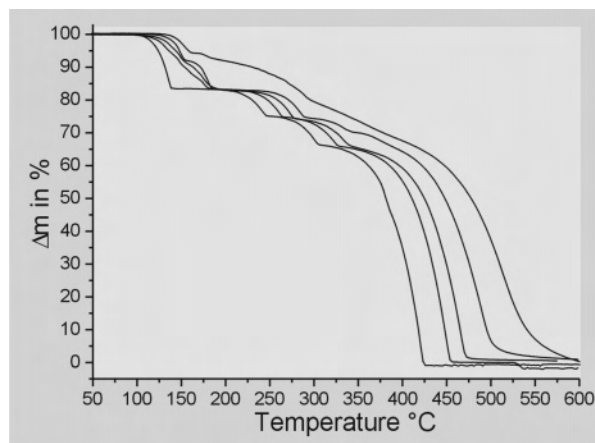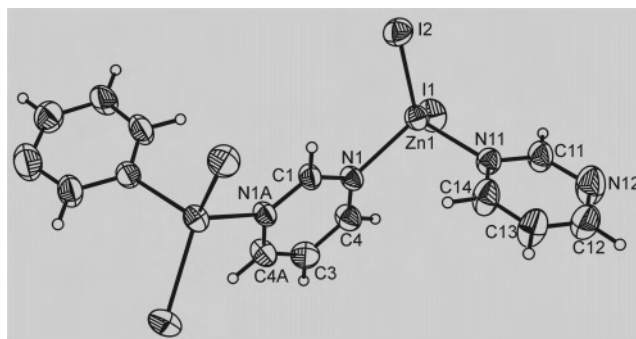
Single crystals of the new compound **2** can also be grown in solution, and structural analysis shows that a 2:3 compound has formed, which crystallizes in space group $C2/c$ with $Z = 4$ and all atoms in general positions. The structure of the 2:3 compound **2** consists of discrete $(ZnI_2)_2$-(pyrimidine)$_3$ units, in which each of the two the zinc atoms are coordinated by one terminal and one bridging pyrimidine ligand (Figure 7). These units are located on the centers of inversion. Bond lengths and angles of **2** are in good agreement with those of **1** and are comparable to values retrieved from the literature (Table 2). The formation of compound **2** as an intermediate in the thermal reaction of compound **1** was further confirmed by comparing the experimental PXRD pattern of the residue formed in the thermal reaction with that calculated from single-crystal data (Figure 4).

From a structural point of view, compound **2** represents an intermediate for the transformation of the tetrahedral discrete ZnI_2(pyrimidine)$_2$ units in compound **1** into the infinite ZnI_2(pyrimidine) chains in the 1:1 compound **3**. Interestingly, a detailed analysis of the crystal structures of compounds **1**−**3** reveals a smooth reaction pathway for the transformation of **1** into **3** via **2**, which requires only small rotational and translational steps (Figure 8). This clearly indicates that there are some three-dimensional similarities, even if a topotactic reaction pathway is unlikely.

In further experiments, we investigated the reaction of zinc iodide with pyrimidine in acetonitrile as described in the
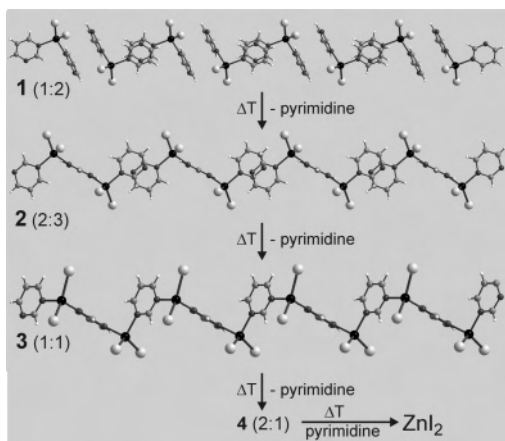
Figure 8. Structural aspects of the thermal decomposition reaction of compound **1** into **3** via **2** as the intermediate.

beginning, but this reaction was quenched by the addition of an antisolvent (see the Experimental Section). Surprisingly, the PXRD pattern of the precipitate does not correspond to those of compounds **1**−**4**. Elemental analysis shows that the composition corresponds approximately to that of a new 1:1 compound (**5**). Single crystals of this compound can also be grown from solution, by evaporating the solvent at different rates (see below and the Experimental Section). Single-crystal structural analysis of compound **5** shows that the compound has the expected 1:1 composition and in addition contains a small amount of acetonitrile. Compound **5** crystallizes in space group $P4/m$ with eight formula units in the unit cell. The structure consists of ZnI$_2$(pyrimidine) units, in which the zinc atoms are coordinated by two iodine atoms and two pyrimidine ligands within distorted tetrahedra (Figure 9, top, and Table 3).

These units are connected by the ligands via μ-N,N′ coordination into [(ZnI$_2$)(pyrimine)]$_4$ rings, which are located on a 4-fold axis.

These rings are stacked in the direction of the c axis, forming channels in which additional solvent molecules are located (Figure 8, bottom).

In further investigations, compound **5** was stored under reduced pressure in order to determine whether the solvent can be deintercalated in a topotactic reaction, but no changes were observed. Therefore, TG/DTA−MS measurements were performed, which show four mass steps. The MS measurements confirm that in the first step only acetonitrile is removed, whereas in the second and third steps half of each of the pyrimidine ligands is emitted (Figure 10). The loss of the CH$_3$CN solvent can be accounted for by the formation of a 1:1 compound, while the loss of the nitrogen donor ligand can be attributed to the formation of the ligand-deficient 2:1 compound **4**.

Surprisingly, the PXRD pattern of the residue formed in the first TG step does not correspond to that calculated for the 1:1 compound **3**, indicating the formation of a new 1:1 compound **6**. In addition, the DSC thermogram exhibits a more complex profile, pointing to the formation of more intermediates (Figure 10). In view of this, the reaction was stopped at different temperatures after the first TG step and
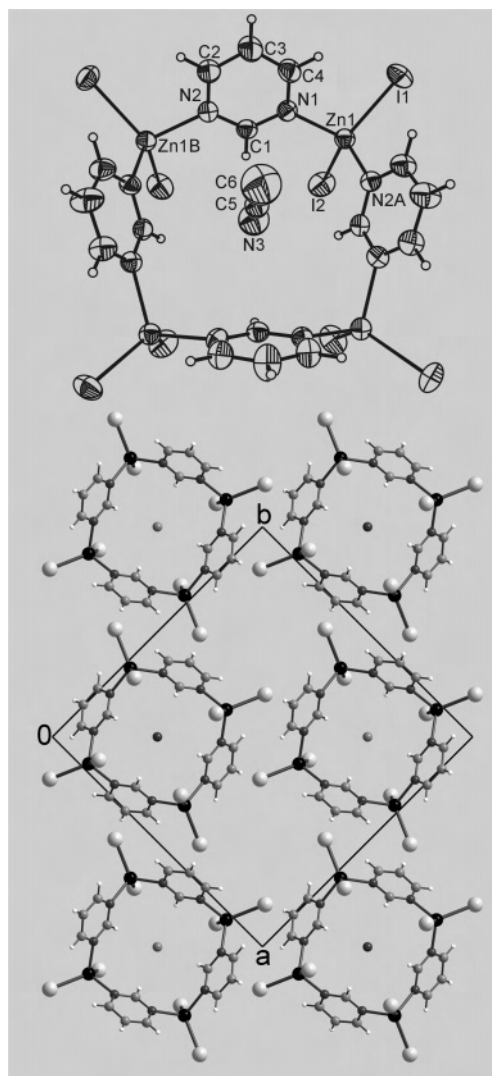

Figure 9. Crystal structure of the 1:1 compound **5** with labeling and displacement ellipsoids drawn at the 50% probability level (top) and with a view along the c axis (bottom).
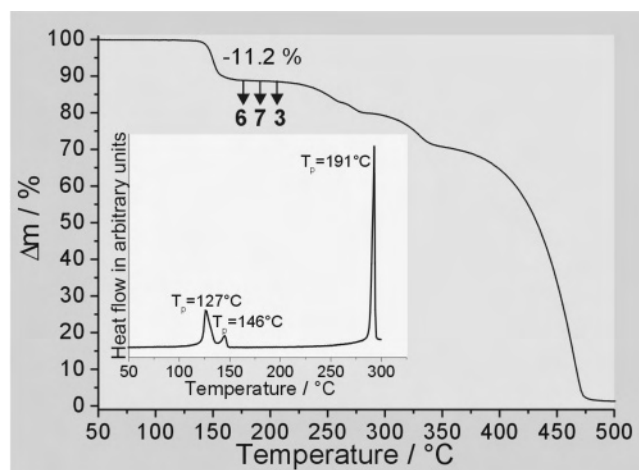

Figure 10. TG curve of compound **5** (the inset shows the DSC curve of this compound).

investigated by PXRD, which shows that, depending on the temperature and where the residues are isolated, three different compounds were obtained. Because the composition of these compounds remains constant, all of them must
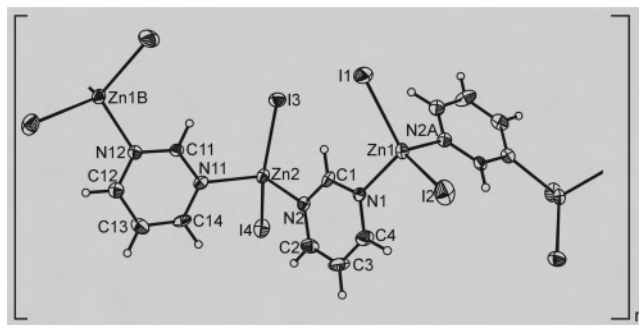
Table 3. Bond Lengths [Å] and Angles [deg] for Compounds **5**−**7**

	Compound **5**		
Zn1−N1	2.104(4)	Zn1−I2	2.5217(8)
Zn1−N2A	2.105(4)	Zn1−I1	2.5307(7)
N2−Zn1B	2.105(4)		
N2A−Zn1−I2	108.70(13)	N2A−Zn1−I1	106.20(12)
N1−Zn1−I1	106.20(12)	I2−Zn1−I1	122.79(3)
	Compound **6**		
Zn1−N1	2.083(5)	Zn2−N2	2.116(5)
Zn1−N12A	2.134(5)	Zn2−N11	2.120(5)
Zn1−I2	2.5005(10)	Zn2−I3	2.5253(9)
Zn1−I1	2.5364(10)	Zn2−I4	2.5660(9)
N12−Zn1B	2.134(5)		
N1−Zn1−N12A	96.8(2)	N2−Zn2−N11	106.57(19)
N1−Zn1−I2	110.06(14)	N2−Zn2−I3	106.25(14)
N12A−Zn1−I2	111.13(15)	N11−Zn2−I3	105.20(14)
N1−Zn1−I1	111.04(15)	N2−Zn2−I4	102.32(14)
N12A−Zn1−I1	105.39(15)	N11−Zn2−I4	99.60(14)
I2−Zn1−I1	119.85(3)	I3−Zn2−I4	134.44(3)
	Compound **7**		
Zn1−N1	2.102(4)	Zn2−N2A	2.101(4)
Zn1−N11	2.107(4)	Zn2−N2	2.101(4)
Zn1−I2	2.5140(7)	Zn2−I4	2.5013(16)
Zn1−I1	2.5276(5)	Zn2−I3	2.5364(7)
N1−Zn1−N11	95.02(14)	N2A−Zn2−N2	96.24(19)
N1−Zn1−I2	108.54(10)	N2A−Zn2−I4	107.77(10)
N11−Zn1−I2	107.67(10)	N2−Zn2−I4	107.77(10)
N1−Zn1−I1	107.41(9)	N2A−Zn2−I3	107.15(9)
N11−Zn1−I1	106.97(10)	N2−Zn2−I3	107.15(9)
I2−Zn1−I1	126.66(3)	I4−Zn2−I3	126.59(3)

Figure 11. Crystal structure of the 1:1 compound **6** with labeling and displacement ellipsoids drawn at the 50% probability level.

represent different modifications of a 1:1 compound. The product isolated at the highest temperature after the first TG step corresponds to the 1:1 compound **3**, also obtained from the thermal decomposition reaction of compound **1**, and the product formed in the second TG step corresponds to the 2:1 compound **4**.

To investigate this reaction in more detail and to identify the two additional intermediates **6** and **7**, several crystallization experiments were performed. In these experiments, the solvent was removed at different rates and the single crystals formed by this procedure were investigated by PXRD. In the PXRD pattern of some of these batches, additional reflections were observed that correspond to those also observed in the PXRD pattern of the intermediates **6** and **7** observed in the thermal decomposition reaction of compound **5**. From these batches, different single crystals were selected, and by this procedure, the crystal structures of compounds **6** and **7** were determined.

The 1:1 compound **6** formed in the beginning crystallizes in space group $P2_1/c$ with $Z = 8$ and two crystallographically independent ZnI_2(pyrimidine) units in the asymmetric unit (Figure 11). In the crystal structure, each zinc atom is connected by two iodine atoms and two pyrimidine ligands and the coordination polyhedron can be described as a distorted tetrahedron (Table 3). Bond lengths and angles are in good agreement with those in compound **3**. The ZnI_2 units are connected via the pyrimidine ligands into chains that elongate in the direction of the c axis. Thus, the topology of the 1:1 compound **6** is identical with that of the 1:1 compound **3**, and both compounds represent polymorphic modifications.

The 1:1 compound **7** crystallizes in space group *Pnma* with $Z = 12$ and 1.5 crystallographically independent ZnI_2-(pyrimidine) units in the asymmetric unit. The zinc and iodine atoms as well as one ligand are located in general positions, and the second ligand occupies a special position. As in all other compounds, the zinc atoms are tetrahedrally coordinated by the iodine atoms and the pyrimidine ligands. In contrast to compounds **3** and **6**, the ZnI_2(pyrimidine) units are connected into cyclic $[(ZnI_2$(pyrimidine)]_3$ trimers (Figure 12 and Table 3).

On the basis of the structural results, all intermediates in the thermal decomposition reaction of compound **5** were identified. This shows clearly that compound **5** loses the solvent and transforms into the new 1:1 compound **6**, which undergoes two successive polymorphic phase transitions. It is surprising that the $[(ZnI_2$(pyrimidine)]_4$ tetramers in **5** transform into chains (**6**) that reorganize into $[(ZnI_2$-(pyrimidine)]_3$ trimers (**7**) before chains are formed again. It might be more likely that **5** transforms first into **7** before a transformation into chains is observed. However, this can be excluded. Moreover, for a reaction of the tetramers into trimers, no smooth reaction pathway can be found, whereas for the reaction of the tetramers into the chains, only small translational and rotational movements are needed.

In order to determine if compounds **6** and **7** can also be obtained in solution and to prove which of the compounds represents the thermodynamically most stable compounds, crystalline powders formed from different ratios of ZnI_2 and pyrimidine were stirred in acetonitrile for 1 week and afterward identified by PXRD (Table 4). These investigations clearly show that only compounds **1**−**4** can be obtained by this procedure and, therefore, represent the most stable compounds. Compounds **5**−**7** cannot be obtained and, thus, must be metastable.

In order to determine if the polymorphic compounds **6** and **7** are formed by kinetic control, several ex situ time-dependent PXRD measurements were performed (Figure 13). These experiments confirm that compound **6** is initially formed but transforms within a few minutes into compound **7**, which finally transforms within about 1 day into compound **3**. Therefore, forms **6** and **7** are thermodynamically metastable, whereas form **3** is stable.

In this context, it is surprising that single crystals of the metastable compounds **5**−**7** can be grown because one would expect that in solution a transformation into the thermody-
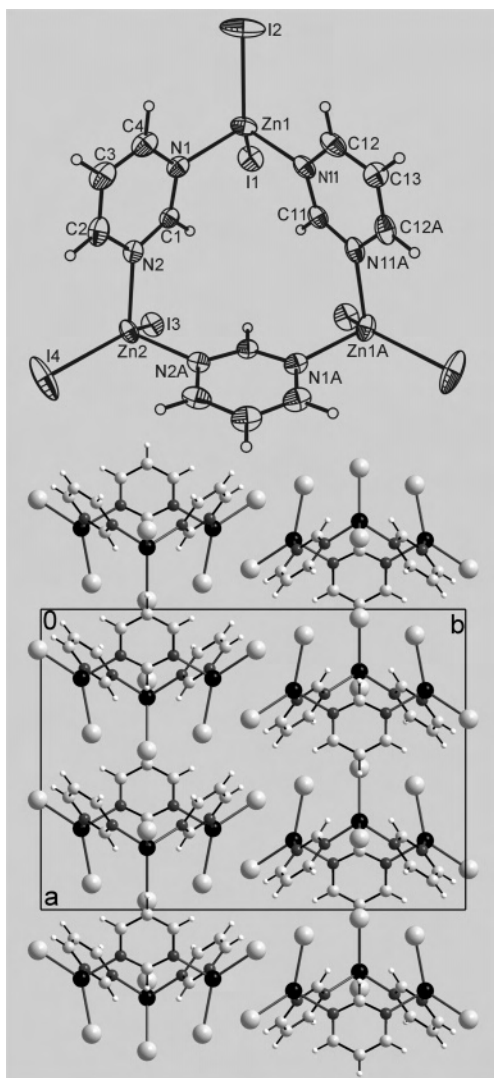
Figure 12. Crystal structure of the 1:1 compound **7** with labeling and displacement ellipsoids drawn at the 50% probability level.

Table 4. Results of the Solvent-Mediated Conversion Experiments If Different Ratios of ZnI$_2$ Are Reacted with Pyrimidine in Acetontrile for 1 Week

	ZnI$_2$/ligand					
	1:3	1:2	2:3	1:1	3:2	2:1
product	**1** (1:2)		**2** (2:3)	**3** (1:1)	**3** (1:1)	**4** (2:1)

namically stable compounds will occur before large crystals are formed. However, in the beginning the thermodynamic, metastable compounds will crystallize, but the transformation can be suppressed if the solution is supersaturated and always new crystal nuclei of the metastable compounds will form. This can be reached if the solvent is quickly evaporated. In this case, the metastable nuclei formed in the beginning will grow continuously. However, this process is difficult to control and, therefore, in the present study a large number of crystallization experiments were performed using different ratios of ZnI$_2$ and pyrimidine, in which the solvent was evaporated at different rates. When sufficient crystals had formed for single-crystal XRD, crystallization was stopped and a part of the crystalline product was investigated by PXRD. In those batches in which reflections of a desired
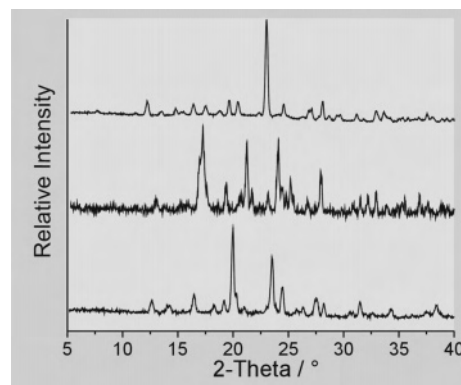
Figure 13. Experimental PXRD pattern of the residue obtained after 5 min (**6**) (top), 30 min (**7**) (middle), and 1 day (**3**) (bottom) if ZnI$_2$ is reacted with pyrimidine in acetonitrile in a ratio of 1:1 (Cu Kα radiation).

compound were identified, several crystals of this batch were checked by single-crystal XRD. There is absolutely no doubt that this procedure is difficult to reproduce but as shown in this work is very effective.

Conclusions

In this contribution, we have reported seven new coordination compounds based on ZnI$_2$ and pyrimidine. We have clearly shown that new stable and metastable coordination compounds can be efficiently discovered and conveniently prepared by thermal decomposition reactions of suitable ligand-rich precursor compounds. In the present case, the seven compounds reported can also be isolated from solution. For the simple reaction of ZnI$_2$ with pyrimidine completely, different products (**1** and **5**) were obtained under thermodynamic or kinetic control, leading to completely different compounds on thermal decomposition (Figure 1). Six of the seven metastable and stable compounds were characterized by single-crystal XRD and, therefore, provide detailed information of the structural aspects of the thermal decomposition reactions. For some of the decomposition reactions, a smooth reaction pathway was found, which provides clear indications that structural information is transferred from the reactants into the products and thus conserved during the reaction.

The thermoanalytical investigations clearly demonstrate that **3** is the thermodynamically most stable 1:1 compound at higher temperatures and that the order of stability is **7** < **6** < **3**. The time-dependent PXRD experiments show that **3** represents the thermodynamically most stable 1:1 compound at room temperature, that **6** and **7** are metastable, and that the order of thermodynamic stability remains constant. In this context, it must be mentioned that the preparation of the metastable compound **6** is difficult to reproduce. Although this compound could be prepared phase pure in solution and by thermal decomposition in the beginning of our investigations, in later investigations it was noted that several batches were contaminated with other phases. This is not an unusual phenomenon and is well-known for metastable polymorphic modifications. If the experimental environment is contaminated with nuclei of the thermodynamic stable forms, the preparation of the metastable forms

is mostly difficult to achieve.[28,29] To solve this problem, systematic investigations on the control of nucleation are essential.[30,31]

Our investigations show that different species are in equillibria in solution, with some of them being thermodynamically stable or metastable. The unambiguous characterization of the different compounds shows that several compounds exist in solution and gives insight into the formation of coordination compounds and polymers. The simple system based on zinc(II) coordination compounds with pyrimidine reported herein can act as a model for more complex reactions, which will proceed via several intermediates. Thus, the present investigations provide more insight into the structural, thermodynamic, and kinetic aspects of the formation of coordination polymers.

Supporting Information Available: Experimental and calculated PXRD patterns for compounds **1**−**3** and **5**−**7**, experimental pattern of the residues obtained in the thermal decomposition reaction of compound **5** and calculated pattern for compounds **3**, **6**, and **7**, and details on the structure determination of compounds **1**−**3** and **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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