

## STRUCTURE OF bis(2-THIOBARBITURATE)TRIS (2,2-BIPYRIDYL)NICKEL(II) HEXAHYDRATE

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The [Ni(Bipy)<sub>3</sub>](Htba)<sub>2</sub>·6H<sub>2</sub>O (**I**) complex (Bipy is 2,2'-bipyridyl, H<sub>2</sub>tba is 2-thiobarbituric acid) is synthesized and its structure is determined by single crystal XRD (cif-file CCDC No. 1836529). The crystals of **I** are monoclinic:  $a = 13.6618(6)$  Å,  $b = 23.9441(9)$  Å,  $c = 25.4335(8)$  Å,  $\beta = 93.091(1)^\circ$ ,  $V = 8307.7(5)$ , space group  $P2_1/c$ ,  $Z = 8$ . Via multiple intermolecular N–H···O, O–H···O, and C–H···S hydrogen bonds (HBs), the Htba<sup>−</sup> ions and water molecules form channels within which [Ni(Bipy)<sub>3</sub>]<sup>2+</sup> cations are located. The Bipy molecules and the Htba<sup>−</sup> ions are involved in C–H···O HBs and the  $\pi$ – $\pi$  interaction. The results of the thermal analysis and IR spectroscopy agree with the single crystal XRD data.

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Weak non-covalent interactions, such as hydrogen bonds (HBs) and  $\pi$ – $\pi$  interactions, can largely determine the physicochemical properties of materials [1]. Barbituric acid and its derivatives, in particular 2-thiobarbituric acid (H<sub>2</sub>tba), are important building blocks in supramolecular chemistry [2, 3]. The use of H<sub>2</sub>tba and its derivatives in medicine and biology [4] makes it essential to synthesize and study the structure of new thiobarbituric compounds. 2,2'-Bipyridyl (Bipy) is another important ligand in supramolecular chemistry. The compounds containing [M(Bipy)<sub>3</sub>]<sup>2+</sup> cations (M is transition metal) can possess useful photochemical, photophysical, catalytic, and magnetic properties [1, 5]. For example, [Ni(Bipy)<sub>3</sub>]<sup>2+</sup> complexes exhibit photocatalytic activity [6] and electroactive properties promising for the development of redox flow batteries [7]. The structures of compounds simultaneously containing the [Ni(Bipy)<sub>3</sub>]<sup>2+</sup> cation and 2-thiobarbituric acid or its anions are not yet characterized [8]. In this work, we determined the structure of the [Ni(Bipy)<sub>3</sub>](Htba)<sub>2</sub>·6H<sub>2</sub>O (**I**) complex and studied its IR spectrum and thermal stability.

### EXPERIMENTAL

**Synthesis of [Ni(Bipy)<sub>3</sub>](Htba)<sub>2</sub>·6H<sub>2</sub>O (**I**).** A mixture of 0.10 g (0.69 mmol) of chemically pure H<sub>2</sub>tba, 10 ml of water, and 0.050 g (0.35 mmol) of chemically pure nickel carbonate was heated to 90 °C and kept at this temperature for

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1.5 h. As a result of heating, the solution turned green and a green precipitate formed. 0.162 g (1.04 mmol) of 2,2'-bipyridyl (Aldrich) was added with stirring to the hot mixture, then a small amount of the undissolved precipitate mainly consisting of unreacted nickel carbonate was separated by filtering. The orange filtrate of about 8 ml was cooled and left in air at room temperature (pH  $\approx$  6). Red planar rectangular crystals formed in six days were filtered and dried first between filter paper sheets and then in air until reaching a constant weight. The yield of **I** was  $\approx$  45% (0.142 g). A single crystal suitable for XRD was selected from the bulk precipitate. Complex **I** was also synthesized using the similar technique at a molar ratio Ni(II):Bipy = 1:2, but with a lower yield (30%).

**Single crystal XRD.** A 0.48 $\times$ 0.45 $\times$ 0.13 mm red crystal of **I** was examined at 100 K. The reflection intensities were measured on a Bruker D8 VENTURE single crystal diffractometer (MoK $\alpha$  radiation). Experimental absorption corrections were applied using the SADABS software [9] by multi-scanning. The structure model was determined by direct methods and refined using the SHELXTL software [10]. From the difference electron density maps, the positions of hydrogen atoms of Bipy molecules and Htba $^-$  ions were determined, which were then idealized and refined with reference to the main atoms. The hydrogen atoms of water molecules, except for O(10W), O(11W), and O(12W), were located and their position was refined with restraints on bond lengths. In addition, O(10W) and O(11W) atoms are disordered over two positions and the O(12W) atom has a very large thermal parameter indicating possible disorder.

The main crystallographic characteristics of **I** and the parameters of the experiment are as follows: chemical formula C<sub>38</sub>H<sub>42</sub>N<sub>10</sub>NiO<sub>10</sub>S<sub>2</sub>,  $a = 13.6618(6)$  Å,  $b = 23.9441(9)$  Å,  $c = 25.4335(8)$  Å,  $\beta = 93.091(1)^\circ$ ,  $V = 8307.7(5)$  Å<sup>3</sup>, space group  $P2_1/c$ ,  $Z = 8$ ,  $D_x = 1.466$  g/cm<sup>3</sup>,  $\mu = 0.637$  mm<sup>-1</sup>,  $2\theta_{\max} = 60.15^\circ$ ; 292989 measured reflections, 24364 independent reflections, 15769 reflections with  $F > 4\sigma(F)$ ,  $-19 \leq h \leq 19$ ,  $-33 \leq k \leq 33$ ,  $-30 \leq l \leq 35$ ,  $R_{\text{int}} = 0.1044$ , weight scheme  $w = 1/[\sigma^2(F_0^2) + (0.0612P)^2 + 9.7591P]$ ,  $P = \max(F_0^2 + 2F_c^2)/3$ , 1144 refined parameters,  $R1[F_0 > 4\sigma(F_0)] = 0.0540$ ,  $wR2[F_0 > 4\sigma(F_0)] = 0.1217$ ,  $R1_{\text{all}} = 0.1072$ ,  $wR2_{\text{all}} = 0.1434$ ,  $\text{GOOF} = 1.017$ ,  $\Delta\rho_{\max}/\Delta\rho_{\min} = 0.893/-0.623$  e/Å<sup>3</sup>,  $(\Delta/\sigma)_{\max} < 0.002$ .

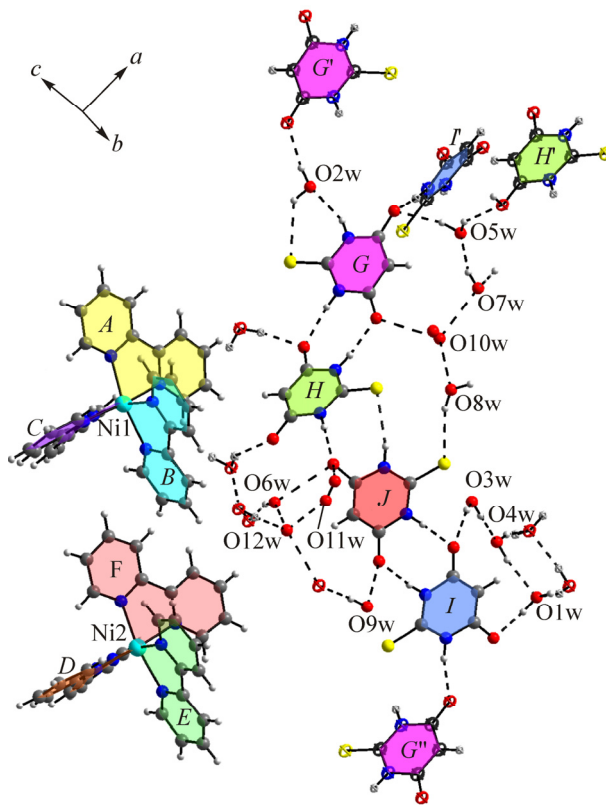
The structure of **I** has been deposited with the Cambridge Structural Database (No. 1836529; deposit@ccdc.cam.ac.uk or [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)). The powder X-ray diffraction pattern of polycrystalline sample of **I** at room temperature (Bruker D8 ADVANCE diffractometer (Multiple-Access Center of the Institute of Physics, Siberian Branch, Russian Academy of Sciences), VANTEC linear detector, CuK $\alpha$  radiation) coincided with that calculated from the single crystal data, which confirmed the identity of the polycrystalline substance and the single crystal examined.

## RESULTS AND DISCUSSION

The asymmetric unit of the unit cell of **I** contains two Ni<sup>2+</sup> ions in general positions 4e, four Htba $^-$  ions, six Bipy molecules, and 12 water molecules in general positions (Fig. 1). Each Ni<sup>2+</sup> ion is coordinated by three Bipy molecules via nitrogen atoms and forms an octahedron; two N atoms from each Bipy molecule close a five-membered ring characteristic of the complexes of this ligand. As a result, the asymmetric unit of the unit cell contains two [Ni(Bipy)<sub>3</sub>]<sup>2+</sup> cations whose charge is compensated by four outer-sphere Htba $^-$  anions. The structure of the complex corresponds to the formula [Ni(Bipy-N,N')<sub>3</sub>]<sub>2</sub>(Htba)<sub>4</sub>·12H<sub>2</sub>O and the name tetrakis(2-thiobarbiturate)bis{tris(2,2-bipyridyl)nickel(II)} dodecahydrate.

The Ni–N bond lengths of 2.055(2)–2.107(2) Å are typical of the Ni<sup>2+</sup> complexes [8]. The Bipy molecules are planar, the N(1)–C(8)–C(7)–N(2) torsion angles range from  $-8.1(3)^\circ$  to  $3.8(3)^\circ$ . The geometric parameters of four independent Htba $^-$  ions ( $G, H, I, J$ ) almost coincide, for example, the C–O bond lengths vary in a range 1.255(3)–1.269(3) Å and those of C–S vary in a range 1.678(3)–1.691(3) Å. The comparison of bond lengths and bond angles in Htba $^-$  suggests the electron density delocalization in O=C–CH–C=O atomic groups previously observed in other metal barbiturates [11, 12].

The analysis of the structure shows the presence of 35 HBs (Table 1) N–H $\cdots$ O, O–H $\cdots$ O, C–H $\cdots$ O, and C–H $\cdots$ S, in which all Htba $^-$  ions and all water molecules are involved. The list of HBs is incomplete because we failed to locate the



**Fig. 1.** Asymmetric unit of the unit cell of  $[\text{Ni}(\text{Bipy})_3](\text{Htba})_2 \cdot 6\text{H}_2\text{O}$ .

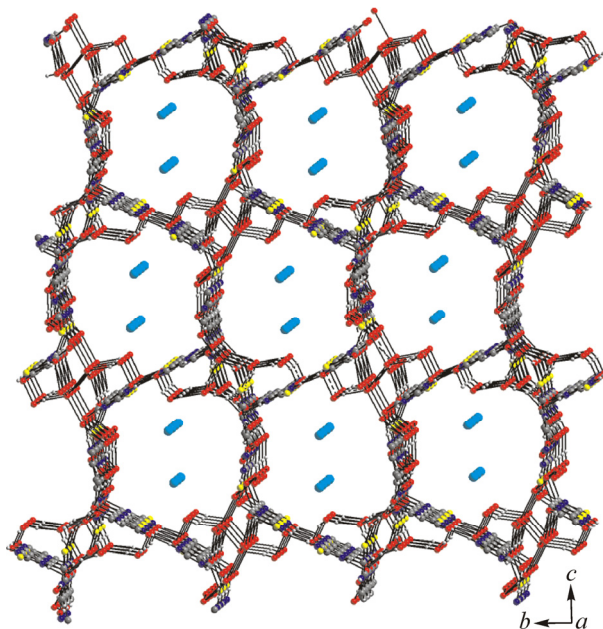
hydrogen atoms of O(10W), O(11W), O(12W) due to disorder of these water molecules. However, the current data on HBs allow us to state the formation of a three-dimensional framework and channels along the  $a$  axis occurring due to HBs (Fig. 2). The diameter of channels running through the structure is about 12.5 Å. Other similar-size  $\text{M}(\text{Bipy})_3^{2+}$  cations can also be expected to form compounds structurally analogous to **I**. The  $\text{N}-\text{H} \cdots \text{O}$  and  $\text{N}-\text{H} \cdots \text{S}$  HBs arrange the independent  $\text{Htba}^-$  ions into  $I$ - $J$ - $H$ - $G$  sequences to form cyclic supramolecular motifs  $R_2^2(8)$ . Each of the terminal  $I$  and  $G$  ions of this four-membered chain is respectively linked by one  $\text{N}-\text{H} \cdots \text{O}$  HB with the  $G'$  and  $I'$  ions of two other four-membered chains. This gives infinite chains of  $\text{Htba}^-$  ions, which are the basis of the whole three-dimensional structure (Fig. 2). For all coordinated Bipy molecules, except for  $D$ , the formation of weak  $\text{C}-\text{H} \cdots \text{O}_{\text{Htba}}$ ,  $\text{C}-\text{H} \cdots \text{OW}$ , and  $\text{C}-\text{H} \cdots \text{S}$  HBs is found. The water molecules are linked together by seven  $\text{OW}-\text{HW} \cdots \text{OW}'$  HBs (Table 1). The  $\pi$ - $\pi$  interaction between the Bipy molecules and the  $\text{Htba}^-$  ions additionally stabilizes the structure of **I**. It should be noted that out of six Bipy molecules ( $A, B, C, D, E, F$ ) only  $C$  and  $D$  are involved in this bonding and out of  $\text{Htba}^-$  ions ( $G, H, I, J$ ) these are only  $I$  and  $J$ . The intercentroid distances vary from 3.513(1) Å to 3.937(2) Å. Each of two adjacent  $I$  and  $J$   $\text{Htba}^-$  ions in the chain linked together by two  $\text{N}-\text{H} \cdots \text{O}$  HBs (Fig. 1) is involved in the  $\pi$ - $\pi$  interaction simultaneously with two aromatic rings of different Bipy molecules, one of which is coordinated to Ni1 and the other is coordinated to Ni2. As a result of stacking interactions, a chain forms that is infinite in the  $c$ - $a$  direction and consists of  $[\text{Ni}(\text{Bipy})_3]^{2+}$  and  $\text{Htba}^-$  ions.

The IR absorption spectrum of **I** in KBr ( $\nu$ ,  $\text{cm}^{-1}$ ) is as follows: 482  $\nu(\text{NiN})$ , 1176  $\nu(\text{CS})$ , 1598 and 1636  $\nu(\text{CO})$ , 2800, 2851, 2927, 2959, 3000, 3066  $\nu(\text{CH})$ , 3106  $\nu(\text{NH})$ , and 3420  $\nu(\text{OH})$ . The IR spectrum (Nicolet 6700, Thermo Scientific, USA; Multiple-Access Center of the Siberian Federal University) of **I** differs from the spectra of the reagents used in the synthesis (Bipy,  $\text{H}_2\text{tba}$ ); it includes bands assigned to the  $\text{Htba}^-$  ion [8, 13] and the coordinated Bipy molecule [14, 15]. The presence of a broad absorption band with a peak at 3420  $\text{cm}^{-1}$  corresponding to  $\nu(\text{OH})$  agrees with the presence of crystallization water in the compound.

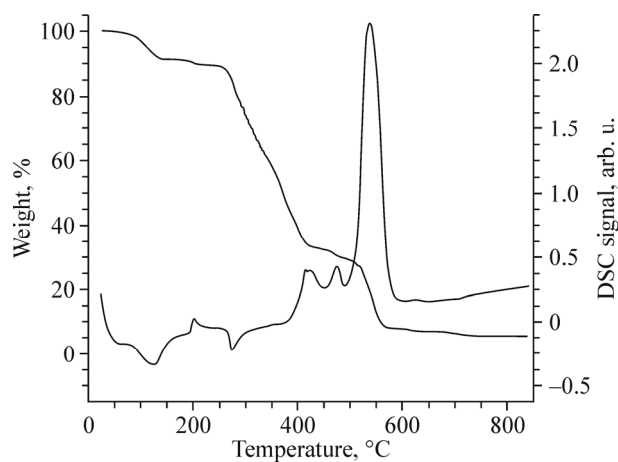
**TABLE 1.** Geometric Parameters of Hydrogen Bonds in the Structure of **I**

D–H···A contact	Distance, Å			DHA angle, deg	Transformation for A atom
	D–H	H···A	D···A		
O(1 <i>W</i> )–H(1 <i>WA</i> )···O(1 <i>I</i> )	0.890(14)	1.849(17)	2.726(3)	168(3)	<i>x, y, z</i>
N(1 <i>G</i> )–H(1 <i>G</i> )···O(2 <i>W</i> )	0.88	2.11	2.940(3)	157	<i>x, y, z</i>
N(1 <i>H</i> )–H(1 <i>H</i> )···O(1 <i>J</i> )	0.88	2.02	2.897(3)	173	<i>x, y, z</i>
N(1 <i>I</i> )–H(1 <i>I</i> )···O(2 <i>J</i> )	0.88	1.92	2.794(3)	172	<i>x, y, z</i>
N(1 <i>J</i> )–H(1 <i>J</i> )···O(2 <i>I</i> )	0.88	1.85	2.725(3)	174	<i>x, y, z</i>
O(1 <i>W</i> )–H(1 <i>WB</i> )···O(1 <i>H</i> )	0.89(2)	1.89(2)	2.777(3)	170(3)	<i>x, 3/2–y, –1/2+z</i>
O(2 <i>W</i> )–H(2 <i>WA</i> )···S(1)	0.884(12)	2.63(2)	3.300(2)	134(2)	<i>x, y, z</i>
N(3 <i>G</i> )–H(3 <i>G</i> )···O(1 <i>H</i> )	0.88	1.92	2.800(3)	173	<i>x, y, z</i>
N(3 <i>H</i> )–H(3 <i>H</i> )···O(1 <i>G</i> )	0.88	1.9	2.771(3)	170	<i>x, y, z</i>
N(3 <i>I</i> )–H(3 <i>I</i> )···O(2 <i>G</i> )	0.88	1.94	2.799(3)	166	<i>–1+x, 3/2–y, –1/2+z</i>
N(3 <i>J</i> )–H(3 <i>J</i> )···S(2)	0.88	2.56	3.374(3)	155	<i>x, y, z</i>
O(2 <i>W</i> )–H(2 <i>WB</i> )···O(2 <i>G</i> )	0.89(2)	1.97(2)	2.846(3)	168(2)	<i>3–x, 1–y, 1–z</i>
O(3 <i>W</i> )–H(3 <i>WA</i> )···O(4 <i>W</i> )	0.892(16)	1.871(15)	2.754(3)	170(3)	<i>x, y, z</i>
O(3 <i>W</i> )–H(3 <i>WB</i> )···O(2 <i>I</i> )	0.90(3)	2.06(3)	2.901(3)	156(2)	<i>x, y, z</i>
O(4 <i>W</i> )–H(4 <i>WA</i> )···O(1 <i>W</i> )	0.89(2)	1.91(2)	2.779(2)	164(2)	<i>2–x, 2–y, –z</i>
O(4 <i>W</i> )–H(4 <i>WB</i> )···O(1 <i>W</i> )	0.888(18)	2.007(19)	2.885(2)	170(2)	<i>x, y, z</i>
O(5 <i>W</i> )–H(5 <i>WA</i> )···O(2 <i>G</i> )	0.91(3)	2.08(3)	2.960(3)	165(4)	<i>x, y, z</i>
O(5 <i>W</i> )–H(5 <i>WB</i> )···O(2 <i>H</i> )	0.91(3)	1.91(3)	2.704(3)	145(3)	<i>1+x, y, z</i>
O(6 <i>W</i> )–H(6 <i>WA</i> )···O(7 <i>W</i> )	0.90(3)	1.85(3)	2.719(4)	161(3)	<i>–1+x, y, z</i>
O(7 <i>W</i> )–H(7 <i>WA</i> )···O(5 <i>W</i> )	0.902(16)	1.95(2)	2.827(4)	163(3)	<i>x, y, z</i>
O(8 <i>W</i> )–H(8 <i>WA</i> )···S(4)	0.92(3)	2.46(4)	3.361(4)	164(4)	<i>x, y, z</i>
O(8 <i>W</i> )–H(8 <i>WB</i> )···O(11 <i>W</i> )	0.92(3)	1.98(4)	2.741(5)	139(3)	<i>2–x, 1–y, –z</i>
O(9 <i>W</i> )–H(9 <i>WA</i> )···O(12 <i>W</i> )	0.90(3)	1.97(3)	2.858(7)	169(5)	<i>1+x, y, z</i>
C(4 <i>C</i> )–H(4 <i>C</i> )···O(2 <i>H</i> )	0.95	2.53	3.467(3)	171	<i>1–x, –1/2+y, 1/2–z</i>
C(4 <i>E</i> )–H(4 <i>E</i> )···O(1 <i>G</i> )	0.95	2.5	3.442(3)	173	<i>1–x, 1/2+y, 1/2–z</i>
C(4 <i>F</i> )–H(4 <i>F</i> )···O(2 <i>H</i> )	0.95	2.34	3.249(3)	160	<i>1–x, 1/2+y, 1/2–z</i>
C(5 <i>F</i> )–H(5 <i>F</i> )···O(6 <i>W</i> )	0.95	2.48	3.133(4)	126	<i>1–x, 1/2+y, 1/2–z</i>
C(5 <i>H</i> )–H(5 <i>H</i> )···O(1 <i>I</i> )	0.95	2.4	3.335(3)	169	<i>x, 3/2–y, –1/2+z</i>
C(6 <i>E</i> )–H(6 <i>E</i> )···O(2 <i>W</i> )	0.95	2.35	3.269(3)	164	<i>–1+x, y, z</i>
C(9 <i>A</i> )–H(9 <i>A</i> )···O(3 <i>W</i> )	0.95	2.51	3.394(3)	156	<i>2–x, –1/2+y, 1/2+z</i>
C(9 <i>B</i> )–H(9 <i>B</i> )···O(9 <i>W</i> )	0.95	2.39	3.303(4)	161	<i>–1+x, y, z</i>
C(9 <i>E</i> )–H(9 <i>E</i> )···O(3 <i>W</i> )	0.95	2.39	3.332(3)	174	<i>–1+x, y, z</i>
C(11 <i>C</i> )–H(11 <i>C</i> )···O(2 <i>W</i> )	0.95	2.5	3.414(3)	160	<i>–1+x, y, z</i>
C(11 <i>E</i> )–H(11 <i>E</i> )···O(1 <i>G</i> )	0.95	2.49	3.351(3)	151	<i>–1+x, y, z</i>
C(11 <i>F</i> )–H(11 <i>F</i> )···S(1)	0.95	2.86	3.472(3)	123	<i>–1+x, y, z</i>
C(12 <i>C</i> )–H(12 <i>C</i> )···O(2 <i>W</i> )	0.95	2.39	3.141(3)	136	<i>2–x, 1–y, 1–z</i>

The thermal analysis of **I** was performed on a SDT-Q600 (TA Instruments, USA) apparatus in an air flow (50 ml/min) in a range 22–850 °C at a heating rate of 10 deg/min. The composition of evolved gases was determined on a Nicolet380 (Thermo Scientific, USA) spectrometer combined with a thermal analyzer. According to the IR spectroscopy data, dehydration of **I** begins at ~70 °C and the endothermic effect at 124.1 °C corresponds to it on the DSC curve (Fig. 3). At 250 °C, the total weight loss of the sample ( $\Delta m_{\text{exp}}$ ) was 10.9%, which is close to the theoretical weight loss calculated in the assumption that all 12 water molecules are removed,  $\Delta m_{\text{calc}} = 11.7\%$ . In a range 250–600 °C, oxidative degradation of the



**Fig. 2.** Three-dimensional structure of channels formed by HBs, in which  $\text{Ni}(\text{Bipy})_3^{2+}$  ions are located.



**Fig. 3.** TG and DSC curves of the thermolysis of **I** in the air atmosphere.

substance occurs which is accompanied by an endothermic effect at 274.5 °C, exothermic effects at 421.8 °C, 474.6 °C, 536.6 °C, and the evolution of gaseous  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{HCN}$ ,  $\text{COS}$ , and  $\text{HNCO}$ . At 600 °C,  $\Delta m_{\text{exp}} = 92.4\%$ , which agrees with the formation of  $\text{NiO}$  ( $\Delta m_{\text{calc}} = 91.9\%$ ) and indirectly confirms the composition of compound **I** determined by single crystal XRD.

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