COORDINATION COMPOUNDS =

[H₄(4,4'-Bipy)₃][Sc(OH)(H₂O)₅]₂Cl₈: Synthesis, Structure, and Solid-Phase Thermal Transformation

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Abstract—The reaction of $[Sc(OH)(H_2O)_5]_2Cl_4 \cdot 2H_2O$ in isopropanol with 4,4'-Bipy in CHCl₃ produced a crystalline compound, which was identified as $[H_4(4,4'-Bipy)_3][Sc(OH)(H_2O)_5]_2Cl_8$ (I) by elemental analysis, IR spectra, and single-crystal X-ray diffraction. In the structure of compound I, the three protonated diimine molecules form a centrosymmetric trimer via N...N hydrogen bonds. The polyhedron around the Sc atom is an octahedron with one split vertex. The excursion of the Sc atom from the plane formed by the oxygen atoms (water molecules) toward the hydroxo bridges is 0.5 Å. The thermolysis of compound I generates ScCl₃, whereas the final decomposition product of the precursor dimer is ScOCl.

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Studies of coordination polymers of scandium sulfates demonstrated the dependence of the supramolecular architecture on ditopic organic cations, such as 4,4'-bipyridine (4,4'-Bipy) [1].

This work studies the influence of structure-forming 4,4'-Bipy on the structural and thermal features of the compound synthesized from the dimer $[Sc(OH)(H_2O)_5]_2Cl_4 \cdot 2H_2O(II)$ [2].

EXPERIMENTAL

Solvents (*i*-PrOH and CHCl₃) and **4,4'-Bipy** were commercially available products and used as received without being purified or dried. A solution of $[Sc(OH)(H_2O)_5]_2Cl_4 \cdot 2H_2O$ in *i*-PrOH, with a scandium concentration of 2.2%, was used in the synthesis. All operations were performed in air.

Elemental analysis for C, H, and N was carried out using standard procedures on a Carlo Erba analyzer at the Shared Facilities Center, Kurnakov Institute of General and Inorganic Chemistry.

IR spectra were recorded as Nujol mulls (KBr cells) on a Nexus Nicolet spectrometer in the range 400–4000 cm⁻¹ at the Shared Facilities Center, Kurnakov Institute of General and Inorganic Chemistry.

The thermolysis of complexes I and II was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) on a Mettler TA-3000 thermal analyzer using DSC-20 and TG-50 units. All experiments were carried out at a constant heating rate of 5 K/min in air. In DSC experiments, test samples were heated in aluminum containers; in TGA experiments, in alundum crucibles. Sample sizes did not exceed 10 mg. Weight change upon heating was monitored directly on a TG-50 unit; the weighing accuracy was $\pm 2 \times 10^{-3}$ mg. The accuracy of determination of anomalous points and peaks on the heat-flow-versustemperature curves was ± 1 K and $\pm 0.5\%$, respectively. X-ray powder diffraction analysis of thermolysis products was carried out on an FR-552 monochromator camera (Cu $K_{\alpha 1}$ radiation) relative to an internal germanium standard (X-ray diffraction patterns were digitized on an IZA-2 comparator with the accuracy ± 0.01 mm) and on a STOE Powder Diffraction System.

Synthesis of $[H_4(4,4'-Bipy)_3][Sc(OH)(H_2O)_5]_2Cl_8$ (I). A solution of 4,4'-Bipy (0.04 g, 0.26 mmol) in CHCl₃ (5 mL) was overlaid with a solution of $[Sc(OH)(H_2O)_5]_2Cl_4 \cdot 2H_2O$ (II) in *i*-PrOH (0.13 mmol Sc) diluted with *i*-PrOH (3 mL). The lower layer clouded; after stirring, the solution became homogeneous. The next day, druses of large crystals appeared in the clear solution. Samples for X-ray structure experiments were chosen from these crystals. The other crystals were separated from the mother solution on a glass filter, washed with CHCl₃, and dried to constant weight over silica gel in a desiccator. Yield: 0.03 g (40% for Sc).

For $C_{30}H_{50}O_{12}N_6Cl_8Sc_2$ (FW = 1060.3) anal. calcd., %: C, 33.98; H, 4.75; N, 7.93.

Found, %: C, 33.63; H, 4.90; N, 7.55.

IR spectrum (cm⁻¹): $v(H_2O)$ 3320, v(NH) 3197, $\sigma(H_2O)$ 1634, $\sigma(ScOH)$ 909, v(ScO) 535, 440.

Compound I was structurally studied (Enraf-Nonius CAD4 diffractometer, MoK_{α} radiation, graphite monochromator, ω scans). The structure was solved by a direct method. The hydrogen atoms of water molecules were found from Fourier electron-difference synthesis. The Bipy hydrogen atoms (at the carbon atoms and one NH atom) were generated geometrically. The structure was refined by the full-matrix least-squares technique in the anisotropic approximation with the fixed hydrogen atoms of water molecules; the Bipy hydrogen atoms were included in the rider model. All calculations were performed using the SHELXS97 [3] and SHELXL97 [4] program packages.

Selected crystal data and the results of structure refinement are listed in Table 1.

The structure data were deposited with the Cambridge Structural Database (CCDC no. 631981).

RESULTS AND DISCUSSION

Compound I was prepared with the ratio 4,4'-Bipy : Sc = 2 (mol/mol). When this ratio decreased to one (with all other synthesis parameters being the same), a crystal phase was not isolated. Moreover, an attempt to use interdiffusion with a 2.5 mL CHCl₃ + 2.5 mL *i*-PrOH interlayer (in the ratio 4,4'-Bipy : Sc = 2 (mol/mol)) yielded crystals that were identified as the salt H₂(4,4'-Bipy)Cl₂ using single-crystal X-ray diffraction [5].

The structure of compound I is built of $[Sc(OH)(H_2O)_5]_2^{4+}$ dimeric cations (Fig. 1a), protonated 4,4'-Bipy cations, and chloride ions. The surrounding of a scandium atom in the cation is irregular; the polyhedron can be described as a pentagonal bipyramid with a strongly nonplane base, but we believe it more reasonable to consider it as an octahedron with one split vertex (hydroxo bridges). Naturally, the scandium atom departs by 0.5 Å from the O(3)-O(6)atomic plane (Fig. 1a) toward the hydroxo bridges. The highest intrinsic symmetry of the complex dimers is *mmm*. This crystallographic symmetry is not crystallographic one in any compound hitherto studied by single-crystal X-ray diffraction. In the precursor salt $[Sc(OH)(H_2O)_5]_2Cl_4 \cdot 2H_2O$, its bromine analogue [2], and $[Sc(OH)(H_2O)_5]_2 \{Na_4(H_2O)_8[calix[4]arene(SO_3)_4]_2\}$. 13H₂O [6], the crystallographic symmetry of the cation is 2/m (in all cases, the scandium atoms and the oxygen atoms of hydroxo bridges lie in plane m). In compound I, the crystallographic symmetry of the cation is -1. Matsumoto et al. [7] determined the structure of the salt $[Sc(OH)(H_2O)_5]_2(PhSO_3)_4 \cdot 2H_2O$ (space group P1), in which the cation symmetry is 1. Ng Seikweng and Hu Shengzhi [8], using the data of Matsumoto et al. [7], heightened the crystal symmetry to C2/c, with the crystallographic symmetry of the cation being 2 (axis 2 is normal to the fragment $\{ \{ Sc(OH) \}_2 \}$.

In crystals, the intrinsic and crystallographic symmetries of $Sc(OH)(H_2O)_5]_2^{4+}$ cations coincide. Figures 1b–1d show the configuration of cations in $[Sc(OH)(H_2O)_5]_2Cl_4 \cdot 2H_2O$ [2], compound I, and $[Sc(OH)(H_2O)_5]_2(PhSO_3)_4 \cdot 2H_2O$ [8], respectively.

Table 1. Selected crystal data and the results of structure re-finement for compound I

Parameter	Value
Formula unit	C ₃₀ H ₅₀ Cl ₈ N ₆ O ₁₂ Sc ₂
Temperature, K	295
Radiation	CuK_{α}
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> , Å	9.2757(12)
b, Å	10.924(2)
<i>c</i> , Å	12.5492(13)
α, deg	84.12(2)
β, deg	77.61(2)
γ, deg	70.63(2)
<i>V</i> , Å ³	1171.0(3)
Ζ	1
$\rho_{calc}, g/cm^3$	1.504
μ , mm ⁻¹	7.202
Crystal size, mm	$0.25\times0.20\times0.15$
θ, deg	3.61-64.94
Reflections collected	4170
Unique reflections	3927
Refined parameters	262
$GOOF(F^2)$	1.024
$R1, wR2 (I > 2\sigma)$	0.0482, 0.1719
R1, wR2 (All reflections)	0.0699, 0.1762

Projection in the Sc...Sc direction highlights what happens with the cation when its intrinsic symmetry changes (for clarity, the hydrogen atoms in the figures are omitted, and the oxygen atoms of the hydroxo bridges are numbered). In transfer from symmetry 2/m to -1, the hydroxo bridges are rotated relative to water molecules (Figs. 1b, 1c); the symmetry of the cations dictates their eclipsed conformation. In $[Sc(OH)(H_2O)_5]_2(PhSO_3)_4 \cdot 2H_2O$, the cation has a trans-conformation [8]. Different conformations are reflected in different Sc-O bond lengths. In the $[Sc(OH)(H_2O)_5]_2X_4 \cdot 2H_2O$ (X = Cl or Br) comcompound pounds [2], I, and $[Sc(OH)(H_2O)_5]_2 \{Na_4(H_2O)_8[calix[4]arene(SO_3)_4]_2 \cdot$ $13H_2O$ [16], the bond lengths are as follows: Sc-O_{OH} 2.03–2.08 Å, Sc– O_w trans to hydroxo bridges, 2.21–2.28 Å; and Sc– O_w 2.17–2.19 Å. In $[Sc(OH)(H_2O)_5]_2(PhSO_3)_4 \cdot 2H_2O$ [8], the bond lengths are as follows: Sc-O_{OH} 2.07 Å, Sc-O_w trans to hydroxo bridges, 2.25 Å; and four Sc-O_w bonds, which the most clustered bonds in the above four compounds, are grouped in pairs (2.14, 2.15, and 2.23×2 Å). There are



Fig. 1. Panel (a): the configuration of the complex cation $[Sc(OH)(H_2O)_5]_2^{4+}$ in the structure of compound **I**. Panels (b–d): the conformation of complex cations $Sc(OH)(H_2O)_5]_2^{4+}$ in the structure of (b) $[Sc(OH)(H_2O)_5]_2Cl_4 \cdot 2H_2O$, (c) compound **I**, and (d) $[Sc(OH)(H_2O)_5]_2(PhSO_3)_4 \cdot 2H_2O$ [8].



Fig. 2. Configuration of a fragment $[H_4(4,4'-Bipy)_3]^{4+}$ in the structure of compound **I**.

no steric hindrances in the cation, and the different conformations are due to stacking factors.

There are 22 hydrogen atoms (20 water molecules and two hydroxo bridges) in the complex cation. All hydrogen atoms of the water molecules are H-bonded: O-H...Cl (Table 2). The hydroxo hydrogen atom is not located; there are two O(1)...Cl contacts (Table 2) that can be regarded as H-bonds.

The protonated diimine molecules are linked into centrosymmetric trimers (Fig. 2) through two N-H...N

H-bonds (Table 2). The hydrogen atom at the nitrogen atom in this H-bond has not been located; most likely, all possible forms of the trimer are in equilibrium at room temperature. The terminal hydrogen atoms are H-bonded: N–H...Cl.

The crystal structure can be derived from a primitive cubic structure: complex cations reside at lattice sites, protonated diimines are in cubic interstices, and chloride ions, so to speak, flow around complex cations

Contact D. H. A	Distance, Å			Angle DNA deg
Contact DIIA	D–H	НА	DA	Aligie DNA, deg
O(1)Cl(1)(-x+1,-y+1,-z+1)			3.269(4)	
O(1)Cl(3)(-x+1, -y, -z+1)			3.355(4)	
O(2)-H(2)Cl(2)(-x + 1, -y, -z + 1)	0.84	2.32	3.146(3)	171
O(2)–H(3)Cl(2)	0.87	2.32	3.168(3)	166
O(3)–H(4)Cl(3)	0.96	2.20	3.064(3)	149
O(3)-H(5)Cl(3)(-x, -y + 1, -z + 1)	0.60	2.60	3.165(3)	160
O(4)–H(6)Cl(2)	1.00	2.19	3.106(4)	151
O(4)-H(7)Cl(1)(-x+1, -y+1, -z+1)	0.86	2.31	3.014(4)	139
O(5)-H(8)Cl(3) (x + 1, y, -z)	0.92	2.19	3.088(3)	165
O(5)-H(9)Cl(2)(-x + 1, -y, -z + 1)	0.50	2.62	3.103(4)	163
O(6)-H(10)Cl(1)	1.05	2.00	3.055(4)	174
O(6)-H(11)Cl(4)	0.90	2.11	3.000(4)	168
N(1)N(3)			2.760(5)	
N(2)–H(2)BCl(4) ($x, y + 1, -z$)	0.86	2.38	3.072(5)	138

Table 2. Hydrogen-bond geometry in the structure of compound I

(Fig. 3). Cationic and anionic layers are distinguished in the structure.

The study of the behavior of aquascandium species in water and crystals [9] showed that the cation



Fig. 3. Projection of the structure of compound I along axis *x*.

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Fig. 4. (a) Heat flow and (b) weight change vs. temperature upon heating of $[Sc(OH)(H_2O)_5]_2Cl_4 \cdot 2H_2O$.

 $[Sc(OH)(H_2O)_5]_2^{4+}$ is one of the most stable species. The same should hold for water–alcohol solutions, which is verified by the synthesis of compound I and the salts $[Sc(OH)(H_2O)_5]_2X_4 \cdot 2H_2O$ (X = Cl or Br) [2].

We studied the solid-phase thermolysis of $[Sc(OH)(H_2O)_5]_2Cl_4 \cdot 2H_2O$. The thermolysis occurs in stages. Before 78°C, the sample loses 2.0% of its weight with energy absorption (a shoulder at the first endotherm; Fig. 4). At 78.5 $\pm 1.0^{\circ}$ C, melting occurs with further degradation. The weight loss at the first stage (67–100°C) is $7.7 \pm 1.0\%$, which corresponds to the percentage of outer-sphere water (calcd., 7.47%). Thus, the first stage is dehydration with attendant melting. The second stage (107-200°C) occurs in two welldefined steps. The first step is at 107-152°C and the second one at 159–200°C, both with energy absorption and the weight loss at each step equal to 18.75%. The total weight loss at the second stage is $37.5 \pm 1.0\%$ (the calculated percentage of coordinated water is 37.34%); this means that the second stage can be considered as deaquation. The third stage occurs at 201–220°C. The weight loss at this stage is $(15.1 \pm 1.0)\%$. Probably, the relevant process is the final destruction of the dimeric complex cation, accompanied by the elimination of two hydrogen chloride moles (the calculated 2HCl percentage is 15.10%). The overall weight loss in the range 67– 220° C is $(60.3 \pm 1.5)\%$. Above 220° C, processes with a change in energy occur, with the weight remaining virtually constant; these processes are usually associated with the structure formation of the final solid product. The phase composition of the solid product was determined by X-ray powder diffraction (Table 3); scandium oxochloride was the only compound detected in the final solid product to the error of X-ray powder diffraction (3.0 wt %). The final product weight is (39.7 \pm 1.5)% of the weight of the starting salt sample (the calculated ScOCl percentage in the salt is 40.04%).

When compound I is heated, processes associated with energy evolution, but not with weight change, are observed in the range 45–75°C. Evidently, we are dealing with the dissociation of multiple hydrogen bonds (the first exotherm; Fig. 5a).

The first thermolysis stage in the range 75–105°C occurs with energy absorption (the second endotherm) and a weight loss of $(6.3 \pm 1.0)\%$. This stage, likely, involves the deprotonation of the terminal diimine molecules of the trimer and the elimination of the resulting two hydrogen chloride molecules (calcd., 6.89% HCl). The product is thermally stable up to $132.0 \pm 2.0^{\circ}$ C. Above this temperature, in the range 132–253°C (the second stage), a multistep process occurs with attendant complex energy changes (the third endotherm, which is the superposition of three peaks, and the fourth endotherm). The weight loss during the second stage is $(20.9 \pm 2.0)\%$. Presumably, this stage involves the following processes: the deaquation and full degradation of the complex cation (this process occurs here at higher temperatures than for salt II and by another mechanism), the deprotonation of the central diimine molecule of the trimer, and the generation of two water

ScOCI* Decom		Decomposit	nposition product	
<i>d</i> , Å	I, %	<i>d</i> , Å	I, %	
8.21	100	8.205	100	
3.573	2	3.580	20	
2.649	3	2.645	20	
2.491	1	2.470	10	
1.982	1	1.985	15	
1.885	1	1.865	10	
1.586	1	1.582	5	

Table 3. Phase analysis of the solid decomposition product

of $[Sc(OH)(H_2O)_5]_2Cl_4 \cdot 2H_2O$

Table 4. Phase analysis of the solid decomposition product of $[H_4(4,4'-Bipy)_3][Sc(OH)(H_2O)_5]_2Cl_8$

ScCl [*] ₃		Decomposition product	
<i>d</i> , Å	I, %	<i>d</i> , Å	I, %
5.9481	60	6.005	50
2.8142	100	2.835	100
2.1750	60	2.165	40
2.0771	20	2.070	30
1.893	20	1.885	15
1.8438	80	1.855	60
1.542	60	1.552	40

* JCPDS Powder Diffraction File, card no. 36-1020.

molecules with the participation of hydroxo bridges, which is made possible by the existence of O(1)...Cl contacts. Thus, we can believe that, in the range 132– 253°C, the gaseous thermolysis products are 12 water molecules per molecule of compound I (the calculated water percentage is 20.37%). Above 253 and up to 370°C, systematic weight loss is observed; the resulting weight loss at this stage is (46.1 ± 2.5)%. This process is accompanied by energy absorption (the fifth endotherm; $\Delta H = 353.0$ kJ/mol). From the values of the weight loss (the theoretical 4,4'-Bipy percentage in compound I is 44.15%), the heat of the process $\Delta_{sub}H^{\circ}(4,4'-Bipy) = 106.3 \pm 2.8$ kJ/mol [10]), and the * JCPDS Powder Diffraction File, card no. 45-0975.

temperature range ($T_b(4,4'-Bipy) = 305.2^{\circ}C$ [10]), we can infer that Bipy elimination occurs at this stage. The overall weight loss in the range 75–370°C is (73.3 ± 2.5)%; the percentage of the solid decomposition product is (26.7 ± 2.5)% against the calculated ScCl₃ percentage in compound I equal to 28.58%. The phase composition of the solid product was determined by X-ray powder diffraction (Table 4); within the X-ray powder diffraction accuracy, poorly crystallized scandium trichloride is the only compound in the final thermolysis product. The variations in the heat flow (Fig. 5a) and sample weight (Fig. 5b) at temperatures above 370°C, likely, correspond to the structure forma-



Fig. 5. (a) Heat flow and (b) weight change vs. temperature upon heating of $[H_4(4,4'-Bipy)_3][Sc(OH)(H_2O)_5]_2Cl_8$.

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tion of the final thermolysis product with simultaneous sublimation.

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