Revisiting Sodium Hexafluoroiridates: Perspective Precursors for Electronic, Quantum, and Related Materials

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ABSTRACT: The following salts have been synthesized and structurally characterized: Na₃[IrF₆]-2H₂O (C2/m, a = 6.6327(4), b = 10.0740(6), c = 5.9283(5) Å, β = 122.3880(10)°) and Na₃[IrF₆]-2H₂O (R-3, a = 7.5963(3), b = 7.5963(3), c = 9.0565(4) Å) (for the first time) by single-crystal X-ray diffraction; the unit cell parameters of a tetragonal phase (P4/mmm, a = 5.005(2), c = 10.074(4) Å) of the stable α-Na₂[IrF₆] were determined for the first time; and the unit cell parameters of β-Na₂[IrF₆] (P2₁, a = 9.332(4), c = 5.136(2) Å) and Na₂[IrF₆] (P₂₁/n, a = 5.567(4), b = 5.778(4), c = 8.017(2) Å, β = 90.41(2)°) were determined using powder X-ray diffraction (PXRD). The data of the thermal stability was obtained by differential thermal analysis (DTA) for all substances. The presence of Na₃[IrF₆]-H₂O monohydrate is predicted. H₂[IrF₆] was prepared in a solution and was demonstrated to behave as a strong dibasic acid.

1. INTRODUCTION

Nowadays, paramagnetic complexes of iridium(IV) are considered as promising building blocks for designing electronic and magnetic quantum materials.¹,² Earlier studies were essentially focused on oxoiridates with the principal structural fragment [IrO₆]₈⁻, and these compounds have been demonstrated to possess some intriguing physical properties, such as Mott spin–orbit insulators,³ superconductors,⁴ Weyl semimetallics,⁵–¹⁰ spin liquids and ices,¹¹⁻¹⁵ and ferromagnets with anomalous Hall effect (AHE).¹⁶ With expectations that materials containing [IrF₆]²⁻ fragments also can exhibit specific physical properties, some efforts for the investigation of the electronic structures of (PPh₃)₂[IrF₆]·2H₂O, Zn(viz)₄[IrF₆] (PPh₃)₂[IrCl₆],¹⁸ A₂[IrF₆] (A = Na, K, Rb, Cs), and Ba[IrF₆]¹⁹ as well as the crystal structures of (PPh₃)₂[IrF₆]-2H₂O, Zn(viz)₄[IrF₆] (PPh₃)₂[IrCl₆],¹⁸ Li₂RhF₆, K₂IrF₆,²⁰ Rb₂IrF₆,²¹ Cs₂IrF₆,²² Ca[IrF₆]·2H₂O, Sr[IrF₆]·2H₂O, and Ba[IrF₆]²³ have been undertaken. The most convenient precursor for the synthesis of diverse hexafluoroiridates (IV) involving different cations is the salt Na₃[IrF₆]. As a rule, sodium salts of iridates are well soluble in water and therefore are handy starting compounds for ligand substitution reactions²⁴ as well as cation metathesis.²¹⁻²³ Although Na₃[IrF₆] has been known for a long time and its unit cell parameters have been reported (P32₁, a = 9.34 Å, c = 5.14 Å),²⁵ followed by structural refinement in 2016 (P32₁, a = 9.32858(24) Å, c = 5.13417(19) Å),¹⁸ there are lacunas in the data on the structures of sodium fluoroiridates including the structure of the stable tetragonal phase Na₃[IrF₆]. Anhydrous sodium fluoroiridates (III) and (IV), as well as crystal hydrates commonly occurring on the crystallization of aqueous solutions, lack both powder and single-crystal structural data. These findings suggest that the studies on the preparation and structures of sodium fluoroiridates need to be revised.

2. EXPERIMENTAL SECTION

The PXRD experiments were examined on a DRON-RM4 diffractometer (Cu Kα source, graphite monochromator at the diffracted beam, room temperature, 2θ range 5–60°). The experimental data were processed with PowderCell program v.2.4.²⁶ The data from the powder structural database PDF²⁷ have been used as standards.

The single crystals were examined on an automated Bruker Nonius X8 APEX diffractometer (MoKα radiation 0.71073 Å, graphite monochromator, CCD detector) at 150(2)K. The reflection intensities were measured by ϕ scanning of narrow (0.5°) frames. Absorption is taken into account empirically using the SADABS program.²⁸ Structures were solved by the direct methods of the difference Fourier synthesis and further refined by the full-matrix least-squares method using the SHELXTL package.²⁹ Atomic thermal parameters for non-

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hydrogen atoms were refined anisotropically. The positions of hydrogen atoms for water molecules are not located.

A thermal analysis was performed on an "STA 449 F1 Jupiter" in a platinum crucible under a helium atmosphere in the temperature range 25–500 °C.

3. RESULTS AND DISCUSSION

β-Na2[IrF6] (I) was prepared according to the literature method35 via the treatment of solid Na2[IrCl6] with gaseous fluorine under dynamic heating up to 300 °C in a flow reactor. Na2[IrCl6] was prepared from commercial "IrCl3·2H2O" in few steps ("The Gulidov Krasnoyarsk Non-Ferrous Metals Plant" Open Joint Stock Company, 51.9% iridium) by dissolution in concentrated hydrochloric acid, followed by the addition of the stoichiometric amount of NaCl and concentration to a concentrated hydrochloric acid, followed by the addition of the product. The attempted recrystallization of β-Na2[IrF6] (I) from aqueous solutions yielded single crystals of Na2[IrF6]·2H2O (II) but not those of (I). We expect that they can be prepared by recrystallization from anhydrous HF; however, such an experiment has not been carried out for technical reasons. Then, the powder of (I) has been examined with powder X-ray diffraction (Figure 1).

The powder diffraction pattern of compound β-Na2[IrF6] (I) was simulated by the full-profile technique using the crystal data of an isostructural compound Na2[SiF6]30,31 (Figure 1), as, according to Babel,31 β-Na2[IrF6] belongs to the structural type of Na2[SiF6] (rhombohedral cell, space group P321). The refinement of the unit cell parameters afforded the following values: sp. gr. P321, a = 9.332(4), c = 5.136(2) Å coinciding within uncertainty with the published data.18

It should be noted that the compound β-Na2[IrF6] is metastable and, similar to Na2[SnF6], it is converted to the tetragonal phase stable at room temperature with the progress of time. The diffraction pattern of a sample of β-Na2[IrF6] stored in a closed vial for two years exhibited reflections of the tetragonal phase α-Na2[IrF6]. The refinement of unit cell parameters gave the following data: sp. gr. P42/mnm, a = 5.005(2), c = 10.074(4) Å (Figure 2).

A comparison of α-Na2[IrF6] and β-Na2[IrF6] structures calculated by the Rietveld method using TOPAS v. 6.035

The obtained single crystals of Na2[IrF6]·2H2O (II) were examined by single-crystal XRD. The crystal data of (II) is as follows: C2/m, a = 6.6327(4) Å, b = 10.0740(6) Å, c = 5.9283(5) Å, β = 122.3880(10)° (ICSD #1955565). The powder diffraction pattern of the bulk sample of (II) confirmed the analytical and phase purity of the product.

The interaction of 1.009 g of β-Na2[IrF6] (I) with 10 ml of H+[IrF6]− from the cation exchanger KU-2 in 10 ml of water under stirring for 30 min (100 rpm) afforded a solution of H3[IrF6] (III). After the removal of the resin by filtration, the solution volume was added to 20 ml with the addition of water and the expected concentration C(Ir) was 0.143 M. The resultant solution was titrated with aqueous NaOH to give the proton content C(H+) of 0.289 M; the iridium concentration C(Ir) of 0.120 M was also determined by UV–vis spectroscopy.34 The determined concentration is less than the expected value, apparently, because of the partial sorption of iridium by the cation resin. Alkali titration gave only one equivalence point; hence, the solution is a strong acid in both steps. The reported behavior35 of (III) as a mixture of the strong acid in the first

Figure 1. Powder diffraction pattern of β-Na2[IrF6] (I) and its full-profile refinement.

| substance | bond distances in [IrF6]− (Å) | bond distances in [NaF6] (Å) | calculated density (g/cm³) |
|-----------|-----------------------------|---------------------------|-------------------------|
| α-Na2[IrF6], low temp. | 1.946 | 2.248 | 4.63 |
| β-Na2[IrF6], high temp. | 1.940 | 2.322 | 4.52 |
| average | 1.943 | 2.295 | |
| mean | 1.940 | 2.311 | |

Figure 2. Powder diffraction pattern of a mixture of α-Na2[IrF6] and β-Na2[IrF6] (I) and its full-profile refinement.
two steps and a weak acid in the third step has not been confirmed by us.

As reported in the literature,25 preparations of the crystals of H$_2$[IrF$_6$] (III) appeared to be unsuccessful. We expect that they can be prepared by the crystallization of IrF$_4$ from anhydrous HF; however, such an experiment has not been carried out for technical reasons. The solution of (III) was used by us for the preparation of a series of salts, however, this contribution is related to only the synthesis of sodium salts, including the preparation from the acid (III).

The interaction of an aqueous solution of H$_2$[IrF$_6$] (III) with sodium chloride, followed by a low concentration in the air, gave large yellow crystals that were identified by single-crystal XRD (by the method described below) as Na$_3$[IrF$_6$]·2H$_2$O (IV) (R-3, a = 7.5963(3), b = 7.5963(3), c = 9.8056(4) Å) (ICSD #1955580).

H$_2$[IrF$_6$] + 3NaCl + 2H$_2$O
→ Na$_3$[IrF$_6$]·2H$_2$O + 1/2 Cl$_2$ + 2HCl

The powder diffraction pattern of the product (IV) prepared via interaction of (III) with a threefold excess of sodium chloride perfectly coincides with the pattern predicted from the single-crystal data (Figure 3).

A gentle attempt to slowly remove water from Na$_3$[IrF$_6$]·2H$_2$O (IV) by stepwise heating to 150 °C (step size of 10 °C) with thermal equilibration at 10–30 min resulted in a weight loss of ~3% (theoretical water content 8.76%). According to the PXRD, the sample was an almost pure phase of (IV), so the partial removal of water did not result in an essential structural rearrangement of (IV). On heating up to 450 °C, the sample completely lost water within the temperature range of 135–400 °C, and underwent further slow partial decomposition (not more than 5%; Figure 4).

Na$_3$[IrF$_6$]·2H$_2$O → Na$_3$[IrF$_6$]·H$_2$O + H$_2$O ↑ (t = 135 – 185 °C)
Na$_3$[IrF$_6$]·2H$_2$O → Na$_3$[IrF$_6$] + H$_2$O ↑ (t = 200 – 400 °C)

2Na$_3$[IrF$_6$] → 6NaF + 2Ir + 3F$_2$ ↑ (t > 380 °C)
4Na$_3$[IrF$_6$] + 6H$_2$O
→ 12NaF + 4Ir + 12HF + 3O$_2$ ↑ (t > 380 °C)

PXRD has demonstrated that the thermal decomposition of Na$_3$[IrF$_6$]·2H$_2$O (IV) mostly afforded Na$_3$[IrF$_6$] (V). In addition to sodium hexafluoiridate, the sample exhibited diffraction peaks of NaF and metallic Ir (Figure 5). The crystallographic data for the salt Ca$_3$TeO$_6$, isostructural to previously unknown Na$_3$[IrF$_6$] (V), were used for full-profile fitting of the unit cell parameters of compound (V): sp. gr. $P2_1/n$, $a = 5.567(4)$, $b = 5.778(4)$, $c = 8.017(2)$ Å, and $\beta = 90.41(2)$°.

The common scheme of conversion in the Na(H)–Or–F(Cl) system is shown in Figure 6 (Na$_2$[IrCl$_6$], Na$_2$[IrCl$_6$]·2H$_2$O, and Na$_2$[IrCl$_6$]·6H$_2$O).
4. CONCLUSIONS

The following salts have been synthesized and structurally characterized for the first time: \( \text{Na}_2[\text{IrF}_6] \cdot 2\text{H}_2\text{O} (\text{C}_2/m, a = 6.6327(4), b = 10.0740(6), c = 5.9283(5) \text{ Å}, \beta = 122.3880(10)^\circ) \) and \( \text{Na}_3[\text{IrF}_6] \cdot 2\text{H}_2\text{O} (\text{R}-3, a = 7.5963(3), b = 7.5963(3), c = 9.8056(4) \text{ Å}) \) by single-crystal XRD; unit cell parameters for \( \beta\)-\( \text{Na}_2[\text{IrF}_6] (\text{P}_321, a = 9.332(4), c = 5.136(2) \text{ Å}) \) and \( \text{Na}_3[\text{IrF}_6] (\text{P}_2_1/n, a = 5.567(4), b = 5.778(4), c = 8.017(2) \text{ Å}, \beta = 90.41(2)^\circ) \) were determined from powder diffraction data. The crystal system and unit cell parameters of \( \beta\)-\( \text{Na}_2[\text{IrF}_6] \) coincide within experimental uncertainty with those of Hepworth,\(^{25}\) and newer results: sp. gr. \( \text{P}_321, a = 9.332(4) \text{ Å}, c = 5.136(2) \text{ Å} \). The unit cell parameters of the stable tetragonal phase \( \alpha\)-\( \text{Na}_2[\text{IrF}_6] (\text{P}_4_2_1/\text{mm}, a = 5.005(2), c = 10.074(4) \text{ Å}) \) were determined for the first time. \( \text{H}_2[\text{IrCl}_6] \) was prepared in solution; and it was demonstrated to behave as a strong dibasic acid. The outline of the thermal decomposition curve suggests the presence of \( \text{Na}_3[\text{IrF}_6] \cdot \text{H}_2\text{O} \). The common scheme of the conversion in \( \text{Na}(\text{H})\text{IrF}^{\text{(I)}} \) was described.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02722.

- Structure of \( \text{Na}_2[\text{IrF}_6] \cdot \text{H}_2\text{O} \) (CIF)
- Structure of \( \text{Na}_3[\text{IrF}_6] \cdot 2\text{H}_2\text{O} \) (CIF)

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Notes

The authors declare no competing financial interest.

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