Supporting Information

Mixed Noble-Gas Compounds of Krypton(II) and Xenon(VI); [F₅Xe(FKrF)AsF₆] and [F₅Xe(FKrF)₂AsF₆]

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Table S1. Experimental geometrical parameters and bond valences (BV) for [F₅Xe(FKrF)AsF₆] (1) and the calculated geometrical parameters for [F₅Xe(FKrF)(AsF₆)]²⁻ (1') and [F₅Xe(FKrF)AsF₆] (1'').

|          | (1)       |         | (1')      |         | (1'')     |         |
|----------|-----------|----------|-----------|----------|-----------|----------|
| distances (Å)[a] | exptl     | BV[b]    | calc      | calc     | calc      | calc     |
| Xe−F1    | 1.8067(11)| 1.25     | 1.919     | 1.893    |           |          |
| Xe−F2    | 1.8394(12)| 1.15     | 1.910     | 1.921    |           |          |
| Xe−F3    | 1.8404(12)| 1.14     | 1.910     | 1.929    |           |          |
| Xe−F4    | 1.8455(13)| 1.13     | 1.909     | 1.910    |           |          |
| Xe−F5    | 1.8462(12)| 1.13     | 1.910     | 1.910    |           |          |
| ΣXe−F    | 5.80      |          |           |          |          |          |
| Xe---F13(Kr) | 2.5139(9) | 0.19     | 2.500     | 2.602    |           |          |
| ΣXe−F+F  | 5.99      |          |           |          |          |          |
| Xe---F9(Asi) | 3.0572(11)| 0.04     | 2.828     | -        |           |          |
| Xe---F10(Asi) | 2.9147(10)| 0.06     | 2.802     | -        |           |          |
| Xe---F11(As) | 2.5944(10)| 0.15     | 2.468     | 2.505    |           |          |
| Xe---F6(As) |          |          |           |          | 2.512     |          |
| ΣXe−FAs   | 0.25      |          |           |          |          |          |
| ΣXe−F+ΣXe−FAs | 6.24     |          |           |          |          |          |
| As−F6    | 1.7029(10)| 0.80     | 1.741     | 1.847    |           |          |
| As−F7    | 1.7039(12)| 0.80     | 1.746     | 1.737    |           |          |
| As−F8    | 1.7051(12)| 0.79     | 1.751     | 1.738    |           |          |
| As−F9    | 1.7130(11)| 0.78     | 1.750     | 1.719    |           |          |
| As−F10   | 1.7301(9) | 0.74     | 1.739     | 1.716    |           |          |
| As−F11   | 1.7559(10)| 0.69     | 1.844     | 1.830    |           |          |
| ΣAs−F    | 4.60      |          |           |          |          |          |
| Kr1−F12  | 1.8393(12)| 1.12     | 1.860     | 1.858    |           |          |
| Kr1−F13  | 1.9367(9) | 0.86     | 1.939     | 1.939    |           |          |
| ΣKr−F    | 1.98      |          |           |          |          |          |
| Asi−F6i  | 1.7029(10)|          | 1.753     |          |           |          |
| Asi−F7i  | 1.7039(12)|          | 1.755     |          |           |          |
| Asi−F8i  | 1.7051(12)|          | 1.761     |          |           |          |
| Asi−F9i  | 1.7130(11)|          | 1.787     |          |           |          |
| Asi−F10i | 1.7301(9) |          | 1.749     |          |           |          |
| Asi−F11i | 1.7559(10)|          | 1.758     |          |           |          |
| Asi−F6ii | 1.7029(10)|          | 1.758     |          |           |          |
| Asi−F7ii | 1.7039(12)|          | 1.754     |          |           |          |
| Asi−F8ii | 1.7051(12)|          | 1.760     |          |           |          |
| Asi−F9ii | 1.7130(11)|          | 1.753     |          |           |          |
| Asi−F10ii| 1.7301(9) |          | 1.789     |          |           |          |
| Asi−F11ii| 1.7559(10)|          | 1.747     |          |           |          |

continued ...
| angles (°) | (1) | (1') | (1'') |
|-----------|-----|------|-------|
| **F1−Xe−F2** | 80.16(7) | 78.1 | 79.3 |
| **F1−Xe−F3** | 79.76(7) | 78.2 | 79.2 |
| **F1−Xe−F4** | 79.70(7) | 77.9 | 80.6 |
| **F1−Xe−F5** | 79.90(7) | 77.8 | 80.2 |
| **F1−Xe−F9**<sup>i</sup> | 124.67(6) | 128.5 | - |
| **F1−Xe−F10**<sup>i</sup> | 129.90(6) | 128.9 | - |
| **F1−Xe−F11** | 146.48(6) | 141.1 | 151.1 |
| **F1−Xe−F13** | 143.54(6) | 142.1 | 130.4 |
| **F2−Xe−F3** | 87.55(6) | 84.9 | 94.0 |
| **F2−Xe−F4** | 89.33(6) | 88.2 | 86.3 |
| **F2−Xe−F5** | 160.06(6) | 155.9 | 158.9 |
| **F2−Xe−F9**<sup>i</sup> | 131.93(5) | 130.1 | - |
| **F2−Xe−F10**<sup>i</sup> | 66.06(5) | 65.9 | - |
| **F2−Xe−F11** | 123.83(5) | 127.6 | 89.2 |
| **F2−Xe−F13** | 75.16(5) | 74.3 | 66.5 |
| **F3−Xe−F4** | 159.45(6) | 156.0 | 159.4 |
| **F3−Xe−F5** | 88.63(6) | 87.9 | 86.9 |
| **F3−Xe−F9**<sup>i</sup> | 62.24(5) | 65.6 | - |
| **F3−Xe−F10**<sup>i</sup> | 131.27(5) | 129.8 | - |
| **F3−Xe−F11** | 120.39(5) | 126.8 | 128.3 |
| **F3−Xe−F13** | 72.85(5) | 73.8 | 69.0 |
| **F4−Xe−F5** | 87.42(6) | 89.1 | 85.6 |
| **F4−Xe−F9**<sup>i</sup> | 131.66(5) | 133.6 | - |
| **F4−Xe−F10**<sup>i</sup> | 64.71(4) | 66.4 | - |
| **F4−Xe−F11** | 77.81(5) | 74.9 | 72.3 |
| **F4−Xe−F13** | 125.75(4) | 126.1 | 128.9 |
| **F5−Xe−F9**<sup>i</sup> | 61.72(5) | 65.9 | - |
| **F5−Xe−F10**<sup>i</sup> | 129.09(5) | 133.8 | - |
| **F5−Xe−F11** | 74.59(5) | 74.5 | 106.8 |
| **F5−Xe−F13** | 122.14(5) | 125.4 | 132.5 |
| **F9−Xe−F10**<sup>i</sup> | 105.41(3) | 102.6 | - |
| **F9−Xe−F11** | 59.41(4) | 61.3 | - |
| **F9−Xe−F13** | 61.14(3) | 59.7 | - |
| **F10<sup>i</sup>−Xe−F11** | 58.95(3) | 61.9 | - |
| **F10<sup>i</sup>−Xe−F13** | 61.44(3) | 59.8 | - |
| **F11−Xe−F13** | 69.81(3) | 76.8 | 65.3 |
| **Kr1−F13---Xe** | 133.24(5) | 121.2 | 125.9 |
| **As−F11---Xe** | 152.97(6) | 139.5 | 106.8 |
| **As<sup>i</sup>−F9<sup>i</sup>---Xe** | 157.25(6) | 139.7 | - |
| **As<sup>ii</sup>−F10<sup>i</sup>---Xe** | 148.84(5) | 139.7 | - |

continued ...
Table S1. (continued)

|                  | (1)    | (1')   | (1'')  |
|------------------|--------|--------|--------|
| angles (°)[a]    | exptl  | calcd  | calcd  |
| F6−As−F7        | 91.26(7) | 90.1   | 87.1   |
| F6−As−F8        | 90.47(7) | 89.6   | 86.0   |
| F6−As−F9        | 91.75(6) | 91.8   | 89.8   |
| F6−As−F10       | 178.06(6) | 176.3  | 173.7  |
| F6−As−F11       | 89.73(5) | 88.1   | 83.0   |
| F7−As−F8        | 176.98(7) | 175.5  | 171.2  |
| F7−As−F9        | 91.33(7) | 91.4   | 92.4   |
| F7−As−F10       | 89.38(6) | 90.3   | 92.9   |
| F7−As−F11       | 88.58(6) | 86.9   | 87.8   |
| F8−As−F9        | 91.09(7) | 92.1   | 93.0   |
| F8−As−F10       | 88.81(6) | 89.6   | 93.4   |
| F8−As−F11       | 88.95(6) | 88.6   | 86.0   |
| F9−As−F10       | 90.06(5) | 91.9   | 96.5   |
| F9−As−F11       | 178.52(5) | 179.3  | 172.8  |
| F10−As−F11      | 88.46(5) | 88.3   | 90.7   |
| F12−Kr1−F13     | 178.49(6) | 176.7  | 178.3  |
| F6−As−F7’       | 91.26(7) | 90.0   |        |
| F6−As−F8’       | 90.47(7) | 89.3   |        |
| F6−As−F9’       | 91.75(6) | 89.9   |        |
| F6−As−F10’      | 178.06(6) | 179.2  |        |
| F6−As−F11’      | 89.73(5) | 90.3   |        |
| F7−As−F8’       | 176.98(7) | 178.0  |        |
| F7−As−F9’       | 91.33(7) | 91.0   |        |
| F8−As−F9’       | 91.09(7) | 88.5   |        |
| F8−As−F10’      | 88.81(6) | 90.3   |        |
| F8−As−F11’      | 88.95(6) | 90.9   |        |
| F9−As−F10’      | 90.06(5) | 89.3   |        |
| F9−As−F11’      | 178.52(5) | 179.3  |        |
| F10−As−F11’     | 88.46(5) | 90.4   |        |
| F6−As−F7”       | 91.26(7) | 91.1   |        |
| F6−As−F8”       | 90.47(7) | 90.9   |        |
| F6−As−F9”       | 91.75(6) | 90.3   |        |
| F6−As−F10”      | 178.06(6) | 179.3  |        |
| F6−As−F11”      | 89.73(5) | 90.5   |        |
| F7−As−F8”       | 176.98(7) | 177.9  |        |
| F7−As−F9”       | 91.33(7) | 90.0   |        |
| F8−As−F9”       | 91.09(7) | 89.6   |        |
| F8−As−F10”      | 88.81(6) | 88.5   |        |
| F8−As−F11”      | 88.95(6) | 90.3   |        |
| F9−As−F10”      | 90.06(5) | 89.9   |        |
| F9−As−F11”      | 178.52(5) | 179.1  |        |
| F10−As−F11”     | 88.46(5) | 90.3   |        |

[a] Symmetry codes: (i) ½−x, y−½, ½−z; (ii) 1−x, 1−y, 1−z.

[b] BV is given in bond valence units (vu) [S1, S2]. The following parameters have been used for the bond valence calculations: \( b = 0.37 \) Å; \( R_0 = 1.88 \) Å (Kr\( ^{VI} \)−F), 1.89 Å (Xe\( ^{VI} \)−F), 1.620 Å (As\( ^{V} \)−F) [S3, S4].
Table S2. Experimental geometrical parameters and bond valences (BV)\(^{[a]}\) for [F\(_{5}\)Xe(FKrF)\(_3\)AsF\(_6\)] (2) and the calculated geometrical parameters for [F\(_{5}\)Xe(FKrF)\(_3\)AsF\(_6\)]\(^{−}\) (2')

|          | (2) exptl | BV\(^{[b]}\) | (2') calcld |
|----------|-----------|-------------|-------------|
| Xe−F1    | 1.8125(15)| 1.23        | 1.911       |
| Xe−F2    | 1.8371(14)| 1.15        | 1.912       |
| Xe−F3    | 1.8418(14)| 1.14        | 1.903       |
| Xe−F4    | 1.8494(14)| 1.13        | 1.909       |
| Xe−F5    | 1.8482(14)| 1.12        | 1.925       |
| Xe−F13(Kr)| 2.5760(15)| 0.16        | 2.626       |
| Xe−F15(Kr)| 2.5449(16)| 0.17        | 2.784       |
| Xe−F10(As)| 3.1236(16)| 0.04        | 2.563       |
| Xe−F11(As)| 2.8117(15)| 0.08        | 2.480       |
| As−F6    | 1.7091(16)| 0.79        | 1.745       |
| As−F7    | 1.7108(16)| 0.78        | 1.750       |
| As−F8    | 1.7126(15)| 0.78        | 1.741       |
| As−F9    | 1.7140(16)| 0.78        | 1.749       |
| As−F10   | 1.7285(14)| 0.75        | 1.737       |
| As−F11   | 1.7433(14)| 0.72        | 1.847       |
| Kr1−F12  | 1.8445(15)| 1.10        | 1.862       |
| Kr1−F13  | 1.9267(15)| 0.88        | 1.930       |
| Kr2−F14  | 1.8505(15)| 1.08        | 1.874       |
| Kr2−F15  | 1.9167(15)| 0.91        | 1.909       |
| As\(^{i}\)−F6\(^{i}\) | 1.7091(16)| 0.79        | 1.740       |
| As\(^{i}\)−F7\(^{i}\) | 1.7108(16)| 0.78        | 1.749       |
| As\(^{i}\)−F8\(^{i}\) | 1.7126(15)| 0.78        | 1.752       |
| As\(^{i}\)−F9\(^{i}\) | 1.7140(16)| 0.78        | 1.752       |
| As\(^{i}\)−F10\(^{i}\) | 1.7285(14)| 0.75        | 1.834       |
| As\(^{i}\)−F11\(^{i}\) | 1.7433(14)| 0.72        | 1.736       |

\(Σ_{Xe−F} = 5.77\)
\(Σ_{Xe−Fb(Kr)} = 0.33\)
\(Σ_{Xe−F} + Σ_{Xe−Fb(Kr)} = 6.10\)
\(Σ_{As−F} = 0.12\)
\(Σ_{Xe−F} + Σ_{As−F} = 6.22\)

\(Σ_{As−F} = 4.60\)
\(Σ_{Kr−F} = 1.98\)
\(Σ_{Kr−F} = 1.99\)

\(Σ_{As−F} = 4.59\)

continued ...
Table S2. (continued)

| angles (°)^[a] | (2)  | (2') |
|----------------|------|------|
| F1–Xe–F2      | 79.28(7) | 77.62 |
| F1–Xe–F3      | 79.84(7) | 78.20 |
| F1–Xe–F4      | 79.71(7) | 77.77 |
| F1–Xe–F5      | 79.47(7) | 77.79 |
| F1–Xe--F10\(i\) | 126.57(6) | 139.81 |
| F1–Xe--F11    | 132.26(6) | 140.53 |
| F1–Xe--F13    | 140.35(7) | 130.55 |
| F1–Xe--F15    | 139.59(7) | 128.26 |
| F2–Xe–F3      | 88.87(7) | 88.04 |
| F2–Xe–F4      | 158.99(7) | 155.37 |
| F2–Xe–F5      | 89.49(7) | 87.09 |
| F2–Xe--F10\(i\) | 131.84(6) | 124.98 |
| F2–Xe--F11    | 66.92(5) | 72.33 |
| F2–Xe--F13    | 129.41(6) | 133.04 |
| F2–Xe--F15    | 73.16(6) | 65.08 |
| F3–Xe–F4      | 87.10(7) | 87.94 |
| F3–Xe–F5      | 159.19(7) | 155.99 |
| F3–Xe--F10\(i\) | 131.16(6) | 129.21 |
| F3–Xe--F11    | 67.26(6) | 75.81 |
| F3–Xe--F13    | 74.90(6) | 67.69 |
| F3–Xe--F15    | 127.56(6) | 131.57 |
| F4–Xe–F5      | 87.04(7) | 86.77 |
| F4–Xe--F10\(i\) | 63.44(6) | 75.14 |
| F4–Xe--F11    | 129.39(6) | 129.79 |
| F4–Xe--F13    | 69.07(6) | 66.63 |
| F4–Xe--F15    | 124.81(6) | 132.54 |
| F5–Xe--F10\(i\) | 62.26(6) | 71.61 |
| F5–Xe--F11    | 130.37(6) | 124.59 |
| F5–Xe--F13    | 121.13(6) | 130.30 |
| F5–Xe--F15    | 71.43(6) | 66.25 |
| F10\(i\)--Xe--F11 | 101.17(4) | 79.39 |
| F10\(i\)--Xe--F13 | 58.90(5) | 61.60 |
| F10\(i\)--Xe--F15 | 61.52(5) | 59.90 |
| F11--Xe--F13  | 62.58(5) | 63.22 |
| F11--Xe--F15  | 60.34(5) | 58.38 |
| F13--Xe--F15  | 79.76(6) | 101.19 |

continued ...
Table S2. (continued)

|             | (2)         | (2')        |
|-------------|-------------|-------------|
| angles (°)[a] | expd        | calcd       |
| Kr1–F13----Xe | 141.80(7)   | 124.71      |
| Kr2–F15----Xe | 137.40(8)   | 123.99      |
| As–F11----Xe  | 144.53(8)   | 138.88      |
| As–F10----Xe  | 136.22(8)   | 144.31      |
| F6–As–F7     | 91.04(10)   | 89.93       |
| F6–As–F8     | 90.33(9)    | 90.18       |
| F6–As–F9     | 178.69(8)   | 174.44      |
| F6–As–F10    | 90.57(8)    | 92.79       |
| F6–As–F11    | 89.86(8)    | 88.21       |
| F7–As–F8     | 178.61(10)  | 174.80      |
| F7–As–F9     | 89.63(10)   | 89.16       |
| F7–As–F10    | 90.21(8)    | 92.38       |
| F7–As–F11    | 89.56(8)    | 87.02       |
| F9–As–F10    | 90.56(8)    | 92.73       |
| F9–As–F11    | 89.02(8)    | 86.26       |
| F10–As–F11   | 179.52(8)   | 178.83      |
| F12–Kr1–F13  | 178.47(8)   | 177.60      |
| F14–Kr2–F15  | 179.40(7)   | 176.98      |
| F6–As–F7     | 91.04(10)   | 90.25       |
| F6–As–F8     | 90.33(9)    | 90.02       |
| F6–As–F9     | 178.69(8)   | 175.25      |
| F6–As–F10    | 90.57(8)    | 88.98       |
| F6–As–F11    | 89.86(8)    | 92.59       |
| F7–As–F8     | 178.61(10)  | 175.03      |
| F7–As–F9     | 89.63(10)   | 89.16       |
| F7–As–F10    | 90.21(8)    | 87.56       |
| F7–As–F11    | 89.56(8)    | 91.15       |
| F9–As–F10    | 90.56(8)    | 86.27       |
| F9–As–F11    | 89.02(8)    | 91.15       |
| F10–As–F11   | 179.52(8)   | 178.43      |

[a] Symmetry codes: (i) x, y+1, z.

[b] BV is given in bond valence units (vu) [S1, S2]. The following parameters have been used for the bond valence calculations: \( b = 0.37 \text{ Å}; R_0 = 1.88 \text{ Å (Kr}^\text{II–F)}, 1.89 \text{ Å (Xe}^\text{VI–F)}, 1.620 \text{ Å (As}^\text{V–F}) [S3, S4].
Figure S5. 

a) The crystal structure of [F₅Xe(FH)AsF₆] (3). The coordination environment of Xe2 is expanded to include symmetry-generated F atoms and [AsF₆]⁻ anions (symmetry codes: (ii) 1−x, y, ½−z; (iii) 1−x, 2−y, 1−z; (iv) x, 2−y, z−½). Thermal ellipsoids are drawn at the 50% probability level. The coordination environment of Xe1 is depicted in Figure 2.

b) A view showing the layered structure in the ac-plane of the unit cell. Black dashed lines denote H⁺···F₆⁻ hydrogen bonds.
Figure S6. The crystal packing and the unit cell of [F₅Xe(FH)AsF₆] (3) viewed along a-axis (top) and the c-axis (bottom) of the unit cell.
Figure S7. a) The crystal structure of [F₂Xe(FH)SbF₆] (4). The coordination environment of Xe is expanded to include symmetry-generated F atoms and [SbF₆]⁻ anions (symmetry codes: (i) 1−x, −y, 1−z; (ii) x, ½−y, z+½). Thermal ellipsoids are drawn at the 50% probability level.

b) A view showing the layered structure in the bc-plane of the unit cell. Black dashed lines denote H⁻⁻⁻Fsb hydrogen bonds.
The asymmetric unit in the crystal structure of 4 is comprised of a \([\text{XeF}_5]^+\) cation, a \([\text{SbF}_6]^−\) anion, and a HF molecule that are all located on general positions (Figure S7a). The Xe(VI) atoms have \(\text{CN}_{\text{Xe}} = 5 + 4\), where the \([\text{XeF}_5]^+\) cation has one shorter secondary Xe---F\(_H\) bond (2.6501(10) Å) and three longer secondary Xe---F\(_\text{Sb}\) bonds that originate from three symmetry-related \([\text{SbF}_6]^−\) anions (2.7065(9), 2.8500(10), and 2.9266(10) Å). Each \([\text{SbF}_6]^−\) anion coordinates to three different \([\text{XeF}_5]^+\) cations in a \textit{mer}-arrangement where the interacting Sb--F bonds are slightly elongated (1.8782(9), 1.8876(9), and 1.8953(9) Å) with respect to the two non-interacting \textit{trans}-Sb--F bonds (1.8607(10), 1.8619(10) Å). The HF molecule is also H-bonded to one neighboring \([\text{SbF}_6]^−\) anion (\(\text{F}_H⋅⋅⋅\text{F}_{\text{Sb}}\), distance 2.5469(14) Å), where the Sb--F bond of the H-bonded F atom (1.9052(9) Å) is the longest of the Sb--F bonds. These secondary Xe---F\(_{\text{Sb}}\) and Xe---F\(_H\) bonding interactions result in layers that are parallel to the \(bc\)-plane of the unit cell and are stacked along the \(a\)-axis (Figure S7b). The anions and cations pack alternatively along the \(c\)-axis of the unit cell (Figures S7, S8).

**Figure S8.** The crystal packing and the unit cell of \([\text{F}_5\text{Xe(FH)SbF}_6]\) (4) viewed along \(c\)-axis (top) and the \(b\)-axis (bottom) of the unit cell.

**X-ray Crystal Structure of \([\text{F}_5\text{Xe(FH)SbF}_6]\) (4)**
Table S3. Experimental geometrical parameters for [F₅Xe(FH)AsF₆] (3) and [F₅Xe(FH)SbF₆] (4)

|          | (3)                |          | (4)                |          |
|----------|--------------------|----------|--------------------|----------|
| distance (Å)[a] | exptl             | distance (Å)[a] | exptl             | distance (Å)[a] | exptl             |
| Xe1−F1   | 1.809(3)           | Xe2−F4   | 1.800(2)           | Xe1−F1   | 1.8129(10)        |
| Xe1−F2   | 1.8379(16)         | Xe2−F5   | 1.8313(16)         | Xe1−F2   | 1.8349(9)         |
| Xe1−F2'  | 1.8379(16)         | Xe2−F5'  | 1.8313(16)         | Xe1−F3   | 1.8372(9)         |
| Xe1−F3   | 1.8352(17)         | Xe2−F6   | 1.8369(16)         | Xe1−F4   | 1.8408(9)         |
| Xe1−F3'  | 1.8352(17)         | Xe2−F6'  | 1.8369(16)         | Xe1−F5   | 1.8423(10)        |
| Xe1−F13(H) | 2.6562(19)   | Xe1−F13(H') | 2.6562(19)  | Xe1−F12(H) | 2.6501(10)        |
| As−F7    | 1.7014(17)         | Sb−F6    | 1.8607(10)         |
| As−F8    | 1.7047(17)         | Sb−F7    | 1.8619(10)         |
| As−F9    | 1.7191(16)         | Sb−F8    | 1.8782(9)          |
| As−F10   | 1.7272(16)         | Sb−F9    | 1.8876(9)          |
| As−F11   | 1.7461(17)         | Sb−F10   | 1.8953(9)          |
| As−F12   | 1.7490(16)         | Sb−F11   | 1.9052(9)          |

|          | (3)                |          | (4)                |          |
|----------|--------------------|----------|--------------------|----------|
| Compound | $D-H\cdots A$[a]   | $D-H$   | H$\cdots A$        | $D\cdots A$ | $D-H\cdots A$ |
| (3)      | F13−H$\cdots$F11   | 0.69(6)  | 1.85(6)            | 2.545(2)  | 176(7)         |
| (4)      | F12−H$\cdots$F11   | 0.876(17)| 1.687(18)          | 2.5469(14)| 166(3)         |

continued …
Table S3. (continued)

| angles (°)[a] | expt | angles (°)[a] | expt | angles (°)[a] | expt |
|--------------|------|--------------|------|--------------|------|
| F1–Xe1–F2   | 80.25(6) | F4–Xe2–F5   | 80.68(5) | F1–Xe1–F2   | 79.65(5) |
| F1–Xe1–F3   | 79.45(6) | F4–Xe2–F6   | 79.95(6) | F1–Xe1–F3   | 79.84(5) |
| F1–Xe1–F2'  | 80.25(6) | F4–Xe2–F5'  | 80.65(5) | F1–Xe1–F4   | 79.60(5) |
| F1–Xe1–F3'  | 79.45(6) | F4–Xe2–F6'  | 79.95(6) | F1–Xe1–F5   | 80.00(5) |
| F1–Xe1–F10  | 134.66(4) | F4–Xe2–F9   | 126.76(3) | F1–Xe1–F8'  | 129.59(4) |
| F1–Xe1–F10' | 134.66(4) | F4–Xe2–F9'  | 126.76(3) | F1–Xe1–F9'  | 131.27(4) |
| F1–Xe1–F13  | 137.23(5) | F4–Xe2–F12'' | 142.72(4) | F1–Xe1–F10  | 139.92(4) |
| F1–Xe1–F13' | 137.23(5) | F4–Xe2–F12'' | 142.72(4) | F1–Xe1–F12  | 139.91(5) |
| F2–Xe1–F3   | 87.71(8) | F5–Xe2–F6   | 88.22(7) | F2–Xe2–F3   | 87.79(5) |
| F2–Xe1–F2'  | 160.51(12) | F5–Xe2–F5'  | 161.35(11) | F2–Xe2–F4   | 159.24(5) |
| F2–Xe1–F3'  | 88.74(8) | F5–Xe2–F6'  | 88.54(7) | F2–Xe2–F5   | 88.37(5) |
| F2–Xe1–F10  | 68.75(7) | F5–Xe2–F9   | 63.73(6) | F2–Xe2–F8'  | 65.08(4) |
| F2–Xe1–F10' | 126.90(7) | F5–Xe2–F9'  | 129.54(6) | F2–Xe2–F9'  | 129.75(4) |
| F2–Xe1–F13  | 126.88(7) | F5–Xe2–F12'' | 72.33(7) | F2–Xe2–F10  | 70.80(4) |
| F2–Xe1–F13' | 69.41(7) | F5–Xe2–F12'' | 124.14(7) | F2–Xe2–F12  | 125.48(4) |
| F3–Xe1–F2'  | 88.74(8) | F6–Xe2–F5'  | 88.54(7) | F3–Xe2–F4   | 89.21(5) |
| F3–Xe1–F3'  | 158.90(13) | F6–Xe2–F6'  | 159.91(11) | F3–Xe2–F5   | 159.84(5) |
| F3–Xe1–F10  | 67.42(7) | F6–Xe2–F9   | 132.79(6) | F3–Xe2–F8'  | 130.18(4) |
| F3–Xe1–F10' | 129.89(7) | F6–Xe2–F9'  | 61.93(6) | F3–Xe2–F9'  | 66.11(4) |
| F3–Xe1–F13  | 70.70(8) | F6–Xe2–F12'' | 74.09(6) | F3–Xe2–F10  | 72.72(4) |
| F3–Xe1–F13' | 126.82(7) | F6–Xe2–F12'' | 124.49(7) | F3–Xe2–F12  | 126.24(4) |
| F2–Xe1–F3'  | 87.71(8) | F5–Xe2–F6'' | 88.22(7) | F4–Xe2–F5   | 87.40(5) |
| F2–Xe1–F10  | 126.90(7) | F5–Xe2–F9'' | 129.54(6) | F4–Xe2–F8'  | 130.13(4) |
| F2–Xe1–F10' | 68.75(7) | F5–Xe2–F9'' | 63.73(6) | F4–Xe2–F9'  | 66.69(4) |
| F2–Xe1–F13  | 69.41(7) | F5–Xe2–F12'' | 124.15(7) | F4–Xe2–F10  | 127.54(4) |
| F2–Xe1–F13' | 126.88(7) | F5–Xe2–F12'' | 72.33(7) | F4–Xe2–F12  | 71.94(4) |
| F3–Xe1–F10  | 129.89(7) | F6–Xe2–F9   | 61.93(6) | F5–Xe2–F8'  | 64.87(4) |
| F3–Xe1–F10' | 67.42(7) | F6–Xe2–F9'  | 132.79(6) | F5–Xe2–F9'  | 129.66(4) |
| F3–Xe1–F13  | 126.82(7) | F6–Xe2–F12' | 123.49(7) | F5–Xe2–F10  | 124.27(4) |
| F3–Xe1–F13' | 70.70(8) | F6–Xe2–F12' | 74.09(6) | F5–Xe2–F12  | 71.23(4) |
| F10–Xe1–F10  | 90.68(7) | F9–Xe2–F9'  | 106.47(6) | F8–Xe2–F9'  | 99.14(3) |
| F10–Xe1–F13  | 58.20(5) | F9–Xe2–F12' | 61.90(5) | F8–Xe2–F10  | 59.44(3) |
| F10–Xe1–F13' | 59.66(5) | F9–Xe2–F12' | 61.22(5) | F8–Xe2–F12  | 60.44(3) |
| F10–Xe1–F13  | 59.66(5) | F9–Xe2–F12' | 61.22(5) | F9–Xe2–F10  | 60.92(3) |
| F10–Xe1–F13' | 58.20(5) | F9–Xe2–F12' | 61.90(5) | F9–Xe2–F12  | 60.16(3) |
| F13–Xe1–F13' | 85.54(10) | F12–Xe2–F12'' | 74.55(7) | F10–Xe2–F12  | 80.13(3) |
| As–F9–Xe1   | 141.60(9) | As–F9–Xe2   | 135.37(9) | Sb–F10–Xe   | 148.79(5) |
| As–F9–Xe1   | 141.60(9) | As–F9–Xe2   | 135.37(9) | Sb–F8–Xe    | 150.01(5) |
| As–F9–Xe2   | 140.08(9) | H–F13–Xe1   | 142(5) | Sb–F9–Xe    | 151.60(5) |
| As–F9–Xe2   | 140.08(9) | H–F13–Xe1   | 142(5) | H–F12–Xe    | 122(2) |
### Table S3. (continued)

|           | (3) angles (°)[a] | (4) angles (°)[a] | exptl | exptl |
|-----------|------------------|------------------|-------|-------|
| F7−As−F8  | 178.15(9)        | F6−Sb−F7        | 179.01(5) |
| F7−As−F9  | 91.22(8)         | F6−Sb−F8        | 89.99(5) |
| F7−As−F10 | 89.95(9)         | F6−Sb−F9        | 89.05(5) |
| F7−As−F11 | 89.32(8)         | F6−Sb−F10       | 90.46(5) |
| F7−As−F12 | 89.46(8)         | F6−Sb−F11       | 90.91(5) |
| F8−As−F9  | 90.59(9)         | F7−Sb−F8        | 90.70(5) |
| F8−As−F10 | 90.40(9)         | F7−Sb−F9        | 90.26(5) |
| F8−As−F11 | 88.85(9)         | F7−Sb−F10       | 90.23(5) |
| F8−As−F12 | 90.17(9)         | F7−Sb−F11       | 88.38(5) |
| F9−As−F10 | 91.09(8)         | F8−Sb−F9        | 179.03(5) |
| F9−As−F11 | 178.42(9)        | F8−Sb−F10       | 91.00(4) |
| F9−As−F12 | 89.85(8)         | F8−Sb−F11       | 90.16(5) |
| F10−As−F11| 90.39(8)         | F9−Sb−F10       | 89.11(4) |
| F10−As−F12| 178.90(9)        | F9−Sb−F11       | 89.76(5) |
| F11−As−F12| 88.67(8)         | F10−Sb−F11      | 178.21(5) |

[a] Symmetry codes: (3) (i) −x, y, ½−z; (ii) 1−x, y, ½−z; (iii) 1−x, 2−y, 1−z; (iv) x, 2−y, z−½; and (4) (i) 1−x, −y, 1−z; (ii) x, ½−y, ½+z; (iii) x,y,z+1.

[b] BV is given in bond valence units (vu) [S1, S2]. The following parameters have been used for the bond valence calculations: \( b = 0.37 \text{ Å} \); \( R_0 = 1.89 \text{ Å} \) (Xe\(^{VI}\)−F), 1.620 Å (As\(^V\)−F), 1.797 Å (Sb\(^V\)−F) [S3, S4].
Figure S9. a) The Raman spectrum of [XeF$_5$][AsF$_6$] starting material recorded at $-141$ °C.

b) The Raman spectrum of [F$_5$Xe(FH)AsF$_6$] (3) recorded at $-150$ °C. Spectra were recorded in FEP sample tubes using 1064-nm excitation. Symbols denote FEP sample tube bands (*) and an instrumental artifact (‡).
Table S4. Experimental Raman Frequencies and Intensities for \([\text{XeF}_5][\text{AsF}_6]\) and \(\text{[F}_5\text{Xe(FH)AsF}_6]\) (3)

| \([\text{XeF}_5][\text{AsF}_6]\)^{[a]} | \([\text{F}_5\text{Xe(FH)AsF}_6]\)^{[a,b]} | \([\text{XeF}_5]^*\) | \([\text{AsF}_6]^*\) |
|---|---|---|---|
| 741(16) | 742(24) | 742, sh |  |
| 725(6) | 726(10) | 711(2) |  \(\nu_3(T_{1u})\) |
| 715(<1) | 712(1) | 709(2) |  |
| 688(20) | 691(23) | 674, sh |  |
| 673(27) | 671(25) | 677(69) |  |
| 664, sh | 670(39), br |  |  |
| 663(26) | 661(23) | 642(42) |  \(\nu_7(E)\) |
| 631(100) | 631(100) | 625(100) |  \(\nu_2(A_1)\) |
| 624(64) | 624(64) | 618(38), br |  |
| 600, sh | 596(<1) | 583, sh |  \(\nu_4(B_1)\)  \(\nu_2(E_g)\) |
| 595(8) | 539, sh | 535(16) |  |
| 536(<1) | 536(<1) | 537(16) |  |
| 411(5) | 412(6) | 413(11) |  \(\nu_8(E)\) |
| 409(3) | 409(3) | 410(9) |  |
| 399(9) | 399(9) | 394, sh |  \(\nu_4(T_{1u})\) |
| 394(9) | 394(9) | 386(4) |  |
| 380(1) | 381(4) | 383(3) |  |
| 375(5) | 374(6) | 374(8) |  \(\nu_5(T_{2g})\) |
| 365(4) | 363(5) | 362(4) |  |
| 346(2) | 348(2) | 344(2) |  \(\nu_3(A_1)\) |
| 349, sh |  |  |  |
| 309(11) | 309(11) | 309(11) |  |
| 304(10) |  |  |  |
| 298(11) | 298(14) | 298, sh |  \(\nu_6(B_2)\) |
| 258(<1) | 255(<1) | 255(<1) |  \(\nu_5(B_1)\) |
| 218(2) | 215(2) | 215(2) |  \(\nu_6(E)\) |
| 130(1) | 138(2) | 138(2) |  |
| 120(2) | 120(2) | 119(4), vbr |  |
| 101(3) | 101(3) | 101(3) |  |

[a] Frequencies are given in cm\(^{-1}\). Values in parentheses denote relative Raman intensities.

[b] The Raman spectrum was recorded in a FEP sample tube at \(-150^\circ\text{C}\) (Figure S9b).

[c] From reference [S5].

[d] This work. The Raman spectrum was recorded in a FEP sample tube at \(-141^\circ\text{C}\) (Figure S9a).
Table S5. Experimental Raman frequencies and intensities for [F₅Xe(FKrF)AsF₆] (1); calculated vibrational frequencies, intensities, and assignments for [F₅Xe(FKrF)(AsF₆)₃]²⁻ (1") and [F₅Xe(FKrF)AsF₆] (1")

| [F₅Xe(FKrF)AsF₆] | [F₅Xe(FKrF)(AsF₆)₃]²⁻ | [F₅Xe(FKrF)AsF₆] |
|------------------|------------------------|------------------|
|                  | expt[a,b,c]            | calcd[d]        | assgnts[e]  | calcd[d]        | assgnts[e]  |
| 719(4)           | 738(<1)[214]           | v(As-F<sub>eq</sub>) | 744(<1)[182] | vs(As-F<sub>cis</sub>) |
|                  | 721(1)[287]            |                  | 739(6)[142] | v<sub>as</sub>(As-F<sub>e</sub>) |
|                  | 718(<1)[307]           |                  | 732(11)[149] | vs(As-F<sub>r</sub>) |
|                  | 713(<1)[57]            |                  |                |                  |
|                  | 703(<1)[256]           |                  |                |                  |
|                  | 701(<1)[46]            |                  |                |                  |
| 693(13)          | 685(20)[30]            | vs(As-F<sub>ax</sub>) | 656(8)[174] | v<sub>as</sub>(Xe-F<sub>eq</sub>) |
|                  | 674(<1)[212]           | v<sub>as</sub>(As-F<sub>ax</sub>) | 652(30)[119] |                  |
|                  | 672(2)[177]            |                  |                |                  |
| 675(63)          | 656(12)[19]            | v(Xe-F<sub>eq</sub>) / v(As-F<sub>eq</sub>) | 656(8)[174] | v<sub>as</sub>(Xe-F<sub>eq</sub>) |
|                  | 653(17)[191]           | v(Xe-F<sub>eq</sub>) / v(As-F<sub>eq</sub>) / v(As-F<sub>ax</sub>) | 652(30)[119] |                  |
|                  | 651(2)[58]             |                  |                |                  |
| 660(5)           | 649(19)[90]            | v(As-F<sub>eq</sub>) | 649(9)[20] | v<sub>as</sub>(As-F<sub>cis</sub>) |
| 650(3)           | 647(5)[347]            | v(Xe-F<sub>eq</sub>) / v(As-F<sub>eq</sub>) | 640(78)[133] | v(Xe-F<sub>ax</sub>) |
| 618(56)          | 624(144)[26]           | vs(As-F<sub>eq</sub>) + v(Xe-F<sub>ax</sub>) | 592(3)[3] | v(As-F<sub>eq</sub>) |
| 533(7)           | 585(7)[186]            | v(Kr-F<sub>i</sub>) | 604(14)[303] | v(Kr-F<sub>i</sub>) |
| 577(<1)          | 577(4)[9]              | v(As-F<sub>eq</sub>) | 573(17)[3] | v<sub>as</sub>(Xe-F<sub>e</sub>) |
| 576(3)[43]       |                        |                  | 582(13)[<1] | v<sub>as</sub>(Xe-F<sub>eq</sub>) |

continued …
Table S5. (continued)

| [F\textsubscript{2}Xe(FKrF)AsF\textsubscript{6}] | [F\textsubscript{2}Xe(FKrF)(AsF\textsubscript{6})\textsubscript{2}] | [F\textsubscript{2}Xe(FKrF)AsF\textsubscript{6}] |
|---------------------------------|------------------------------|---------------------------------|
| exptl\textsuperscript{[a,b,c]} | calcd\textsuperscript{[d]} | assgnst\textsuperscript{[e]} | calcd\textsuperscript{[d]} | assgnst\textsuperscript{[e]} |
| 590(11) | 569(14)[16] | ν(Xe-F\textsubscript{ax}) − ν(Xe-F\textsubscript{4eq})\textsubscript{small} | |
| 549(40) | 547(30)[10] | [ν(As-F\textsubscript{ba}) − ν(Xe-F\textsubscript{ba})] + ν(As-F\textsubscript{ax}) | 535(21)[86] | [ν(As-F\textsubscript{ba}) − ν(Xe-F\textsubscript{ba})]\textsubscript{out-of-phase} − ν(As-F\textsubscript{cis})\textsubscript{small} |
| 540(9) | 544(15)[59] | | | |
| 454(100) | 491(34)[140] | ν(Kr-F\textsubscript{b}) + very minor | 498(60)[104] | ν(Kr-F\textsubscript{b}) |
| [l] | 478(8)[108] | [ν(As-F\textsubscript{ba}) − ν(Xe-F\textsubscript{ba})] + ν(Kr-F\textsubscript{b})\textsubscript{small} | 469(5)[3] | [ν(As-F\textsubscript{ba}) − ν(Xe-F\textsubscript{ba})]\textsubscript{out-of-phase} |
| 411(5) | 391(5)[38] | δ(F\textsubscript{bA}AsF\textsubscript{eq}) − δ(F\textsubscript{ax}AsF\textsubscript{eq}) / ρ\textsubscript{w}(F\textsubscript{eq}AsF\textsubscript{eq}) | 396(1)[54] | δ(F\textsubscript{AsF\textsubscript{ba}}) − δ(F\textsubscript{AsF\textsubscript{ba}}) / ρ\textsubscript{w}(F\textsubscript{cis}AsF\textsubscript{cis}) |
| 407(4) | 385(1)[9] | δ(AsF\textsubscript{ba}F\textsubscript{eq}F\textsubscript{eq}) − δ(AsF\textsubscript{ax}F\textsubscript{eq}F\textsubscript{eq}) | 393(1)[128] | δ(AsF\textsubscript{cis}F\textsubscript{ba}F\textsubscript{ba}) |
| | 383(1)[71] | | 372(1)[80] | δ(AsF\textsubscript{cis}F\textsubscript{ba}F\textsubscript{ba}) − δ(AsF\textsubscript{cis}F\textsubscript{b}F\textsubscript{b})\textsubscript{small} |
| 400(<1) | 381(1)[52] | δ(F\textsubscript{bA}AsF\textsubscript{eq}) − δ(F\textsubscript{ax}AsF\textsubscript{eq}) / ρ\textsubscript{w}(F\textsubscript{eq}AsF\textsubscript{eq}) | | |
| 394(<1) | 380(1)[30] | δ(F\textsubscript{eq}AsF\textsubscript{eq}) − δ(F\textsubscript{eq}AsF\textsubscript{eq}) / ρ\textsubscript{w}(F\textsubscript{ax}AsF\textsubscript{b}) | 361(<1)[1] | δ(F\textsubscript{AsF\textsubscript{ba}}) + δ(F\textsubscript{ba}AsF\textsubscript{ba}) / ρ\textsubscript{w}(F\textsubscript{cis}AsF\textsubscript{cis}) |
| 379(<1) | 379(<0.1)[38] | δ(F\textsubscript{eq}AsF\textsubscript{eq}) − δ(F\textsubscript{eq}AsF\textsubscript{eq}) / ρ\textsubscript{w}(F\textsubscript{ax}AsF\textsubscript{b}) | 367<1>[96] | δ(F\textsubscript{eq}XeF\textsubscript{ax}) |
| | 377(1)<0.1)[96] | | | |
| 376(1)[13] | 372(1)[22] | δ(XeF\textsubscript{eq}F\textsubscript{eq}F\textsubscript{ax}) − δ(XeF\textsubscript{eq}F\textsubscript{eq}F\textsubscript{ax}) | 359(1)[3] | δ(XeF\textsubscript{eq}F\textsubscript{eq}F\textsubscript{ax}) − δ(XeF\textsubscript{eq}F\textsubscript{eq}F\textsubscript{ax}) |
| | 372(1)[60] | | 352(<1)[16] | δ(XeF\textsubscript{eq}F\textsubscript{eq}F\textsubscript{ax}) |
| 368(3) | 369(2)[101] | δ(AsF\textsubscript{4eq})\textsubscript{umb} | | |
| 353(<1)<1] | | δ(F\textsubscript{eq}AsF\textsubscript{eq}) + δ(F\textsubscript{eq}AsF\textsubscript{eq}) | | |
| 347(<1)[27] | | δ(F\textsubscript{ba}AsF\textsubscript{eq}) + δ(F\textsubscript{ax}AsF\textsubscript{eq}) | | |
| 346(<1)[1] | | δ(F\textsubscript{ba}AsF\textsubscript{eq}) + δ(F\textsubscript{ax}AsF\textsubscript{eq}) | | |
| | | | 347(1)[3] | δ(F\textsubscript{ba}AsF\textsubscript{cis}) − δ(F\textsubscript{ba}AsF\textsubscript{cis}) |

continued ...
| [F₂Xe(FKrF)AsF₆] | [F₂Xe(FKrF)(AsF₆)₂]²⁻ | [F₂Xe(FKrF)AsF₆] |
|----------------|-----------------|----------------|
| exptl[a,b,c] | calcd[d] | assgnts[e] | calcd[d] | assgnts[e] |
| 344(3) | 344(1)<1 | 344(1)<1 | 314(1)[66] | δ(XeF₄eq)_{umb} |
| | 342(1)[14] | 340(1)[3] | | 327(1)[75] | δ(XeF₄eq)_{umb} |
| | 340(1)[1] | 330(1)<1 | | 294(4) | δ(FKrF₆)_{g.p.} |
| | 268(2), br | 268(1)[1] | 269(1)[28] | δ(FKrF₆)_{g.p.} |
| | 255(<1) | 264(1)<1 | 264(1)[12] | δ(FKrF₆)_{o.o.p.} / \frac{[\rho_w(F_{eq}XeF_{eq}) - \rho_w(F_{eq}XeF_{eq})]}{δ(F_{eq}XeF_{eq})_{g.p.}} |
| | 251(<0.1)[8] | \frac{[\rho_w(F_{eq}XeF_{eq}) - \rho_w(F_{eq}XeF_{eq})]}{δ(F_{eq}XeF_{eq})_{g.p.}} | 255(1)[1] | \left\{ \frac{[\rho_w(F_{eq}AsF_{eq}) - \rho_w(F_{eq}AsF_{eq})]}{δ(F_{eq}AsF_{eq})_{g.p.}} \right\} |
| | 238(<1), br | 242<1) | 242(1)<1 | 246(1)[17] | δ(FKrF₆)_{o.o.p.} |
| | 226(1) | 242(1)<1 | \frac{[\rho_w(F_{eq}AsF_{eq}) - \rho_w(F_{eq}AsF_{eq})]}{δ(F_{eq}AsF_{eq})_{g.p.}} |
| | 218(0.1)<1 | 226(0.1)<1 | 232(0.1)<2 | \left\{ \frac{[\rho_w(F_{eq}AsF_{eq}) - \rho_w(F_{eq}AsF_{eq})]}{δ(F_{eq}AsF_{eq})_{g.p.}} \right\} |
| | 217(0.1)<1 | 229(0.1)<1 | | \frac{[\rho_w(F_{eq}AsF_{eq}) - \rho_w(F_{eq}AsF_{eq})]}{δ(F_{eq}AsF_{eq})_{g.p.}} |
| | 216(1)[4] | 221(1)<1 | \left\{ \frac{[\rho_w(F_{eq}AsF_{eq}) - \rho_w(F_{eq}AsF_{eq})]}{δ(F_{eq}AsF_{eq})_{g.p.}} \right\} |
| continued ... | | | | |

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Table S5. (continued)

| [F₂Xeq(FKrF)(AsF₆)]²⁻ | [F_5Xeq(FKrF)(AsF₆)₃]²⁻ | [F₂Xeq(FKrF)AsF₆] |
|-------------------------|-------------------------|-------------------|
| **exptl[a,b,c]** | **calcld**[d] | **assgnts**[e] | **calcld**[d] | **assgnts**[e] |
| 200(<1) | 204(<0.1)[2] | [ρₚ(F_2eqAsF_2eq) - ρₚ(F_2eqAsF_2eq)] | 201(<1)[<1] | δ(F_2eqXeF_2eq) - δ(F_2eqXeF_2eq) |
| 195(<0.1)[7] | [δ(F_2eqXeF_2eq) - δ(F_2eqXeF_2eq)] | 185(<1)[3] | [δ(F_2eqXeF_2eq) - δ(F_2eqXeF_2eq)] / ρ(F_KrF_b)small |
| 143(12) | 152(2)[8] | ρₚ(F_KrF_b) | 123(3)[3] | ρₚ(F_KrF_b) |
| 136(1)<[5] | ρₚ(F_axXeF_4eq) / ρₚ(F_KrF_b)small | 109(<1)[<1] | ρₚ(F_2baAsF_2v) |
| 130(6) | 136(1)[2] | ρₚ(F_KrF_b) / ρₚ(F_axXeF_4eq)small | 104(<1)[<1] | ρₚ(F_KrF_b) / ρₚ(F_axXeF_4eq)small |
| 122(<1)[2] | ρₚ(F_axXeF_4eq) | 115(2)[4] | ρₚ(AsF_6) / ρₚ(F_KrF_b)small / ρₚ(F_axXeF_2eq)small |
| 119(7) | 96(<0.1)[<1] | ρₚ(XeF_4eq) / ρₚ(AsF_6) | 92(<1)[9] | coupled deformation mode |
| 90(1)[<1] | ρₚ(AsF_6) / ρₚ(AsF_6) | 78(<1)[<1] | ρₚ(AsF_4eq) / δ(XeF_bAAs) | 74(<1)[<1] | ρₚ(AsF_bA_F_2cis) |
| 74(<1)[<1] | 71(<1)[3] | δ(XeF_bAAs) | 58(1)[<0.1] | δ(XeF_bK) / δ(XeF_bAAs) |

continued …
Table S5. (continued)

| [F₂Xe(FKrF)AsF₆] | [F₂Xe(FKrF)(AsF₆)₂]²⁻ | [F₂Xe(FKrF)AsF₆] |
|------------------|------------------------|------------------|
| expt[ᵃ,b,c]      | calcd[ᵈ]               | assgnst[ᵉ]       |
| 46(<1)[<1]       | 30(1)[<0.1]            | coupled deformation mode |
| 105(7)           | 21(<1)[<1]             |                  |
| 100, sh          |                        | lattice modes    |

[a] Frequencies are given in cm⁻¹.

[b] Values in parentheses denote relative Raman intensities. Abbreviations denote shoulder (sh) and broad (br). The Raman spectrum was recorded in a FEP sample tube at −144 °C using 1064-nm excitation (Figure 3).

[c] The band observed at 464(10) cm⁻¹ is assigned to unreacted KrF₂. The weak bands observed at 567(<1), 564(sh), 474(sh), 472(6), and 466(sh) cm⁻¹ are assigned to [F₂Xe(FKrF)₂AsF₆].

[d] Values in parentheses and square brackets denote calculated Raman intensities (Å⁴ amu⁻¹) and infrared intensities (km mol⁻¹), respectively.

[e] Assignments are for the energy-minimized geometry (C₁) calculated using the APFD/aVDZ(-PP)(Xe, As, Kr)/aVDZ(F) level of theory. Abbreviations denote stretch (ν), bend (δ), rock (ρᵣ), twist (ρₜ), wag (ρₜₚ), umbrella (umb), equatorial (eq), axial (ax), F bridging on the AsF₆ group (Fₐ₉), F cis to an Fₐ₉ atom (Fₐ₉cis), F trans to an Fₐ₉ atom (Fₐ₉trans), in-plane (i.p.), and out-of-plane (o.o.p.). Bond elongations and angle openings are denoted by plus (+) signs, and bond contractions and angle compressions are denoted by minus (−) signs. The in-plane and out-of-plane bending modes are relative to the XeF₄KrF₄-plane, where the atoms labeling scheme corresponds to that used in Figure 1a.

[f] The band overlaps with a KrF₂ or [F₂Xe(FKrF)₂AsF₆] band.
Table S6. Experimental Raman frequencies and intensities for \( [\text{F}_5\text{Xe(FKrF)}_2\text{AsF}_6] \) (2); calculated vibrational frequencies, intensities, and assignments for \( [\text{F}_5\text{Xe(FKrF)}_2(\text{AsF}_6)_2]^{-} \) (2')

| \( [\text{F}_5\text{Xe(FKrF)}_2\text{AsF}_6] \) | \( [\text{F}_5\text{Xe(FKrF)}_2(\text{AsF}_6)_2]^{-} \) |
|---|---|
| expt[a,b,c] | calcd[d] | assgnts[e] |
| 720(2) | \( \nu(\text{As-F}_\text{eq}) \) | 728(<1)[340] 726(<1)[222] 724(1)[56] 716(<1)[143] |
| 687(10) | \( \nu(\text{As-F}_\text{ax}) \) | \( \nu(\text{As-F}_\text{ax}) \) |
| 679, sh | \( \nu(\text{As-F}_\text{ax}) \) | \( \nu(\text{As-F}_\text{ax}) \) |
| 671(31) | \( \nu(\text{As-F}_\text{ax}) + \nu(\text{As-F}_{\text{bA}}) \) | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq}) \) |
| 666(12) | \( \nu(\text{As-F}_\text{eq}) \) | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq}) \) |
| 655(1) | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq}) \) | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq})_{\text{small}} \) |
| 647, sh | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq})_{\text{small}} \) | \( \nu(\text{Xe-F}_\text{eq}) + \nu(\text{Xe-F}_\text{ax}) \) |
| 619(39) | \( \nu(\text{Xe-F}_\text{eq}) + \nu(\text{Xe-F}_\text{ax}) \) | \( \nu(\text{Xe-F}_\text{eq}) + \nu(\text{Xe-F}_\text{ax}) \) |
| 613(17) | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq})_{\text{small}} \) | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq})_{\text{small}} \) |
| 567, sh | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq})_{\text{small}} \) | \( \nu(\text{Kr}_1\text{-F}_{12}) + \nu(\text{Kr}_2\text{-F}_{14}) \) − \( \nu(\text{Kr}_1\text{-F}_{13}) - \nu(\text{Kr}_2\text{-F}_{15}) \)_{\text{small}} |
| 556(5) | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq})_{\text{small}} \) | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq})_{\text{small}} \) |
| 543, sh | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq})_{\text{small}} \) | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq})_{\text{small}} \) |
| 537(12) | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq})_{\text{small}} \) | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq})_{\text{small}} \) |
| 474, sh | \( \nu(\text{Xe-F}_\text{eq}) / \nu(\text{As-F}_\text{eq})_{\text{small}} \) | \( \nu(\text{Kr}_2\text{-F}_{15}) + \nu(\text{Kr}_2\text{-F}_{14})_{\text{small}} \) |
| 472(100) | \( \nu(\text{Kr}_2\text{-F}_{15}) + \nu(\text{Kr}_2\text{-F}_{14})_{\text{small}} \) | \( \nu(\text{Kr}_1\text{-F}_{13}) + \nu(\text{Kr}_1\text{-F}_{12})_{\text{small}} \) |
| 466(83) | \( \nu(\text{Kr}_1\text{-F}_{13}) + \nu(\text{Kr}_1\text{-F}_{12})_{\text{small}} \) | \( \nu(\text{Kr}_1\text{-F}_{13}) + \nu(\text{Kr}_1\text{-F}_{12})_{\text{small}} \) |
| 507(1) | \( \nu(\text{As-F}_{\text{bA}}) \) | \( \nu(\text{As-F}_{\text{bA}}) \) |
| [f] | \( \nu(\text{As-F}_{\text{bA}}) \) | \( \nu(\text{As-F}_{\text{bA}}) \) |
| 418(2) | \( \delta(\text{F}_{\text{bA}}\text{AsF}_{\text{eq}}) - \delta(\text{F}_{\text{ax}}\text{AsF}_{\text{eq}}) / \rho_{\text{w}}(\text{F}_{\text{eq}}\text{AsF}_{\text{eq}}) \) | \( \delta(\text{F}_{\text{bA}}\text{Fe}_{\text{ax}}\text{F}_{\text{eq}}\text{F}_{\text{eq}}) - \delta(\text{F}_{\text{ax}}\text{Fe}_{\text{eq}}\text{F}_{\text{eq}}) \) |
| 405(3) | \( \delta(\text{F}_{\text{bA}}\text{Fe}_{\text{ax}}\text{F}_{\text{eq}}\text{F}_{\text{eq}}) - \delta(\text{F}_{\text{ax}}\text{Fe}_{\text{eq}}\text{F}_{\text{eq}}) \) | \( \delta(\text{F}_{\text{eq}}\text{XeF}_{\text{ax}}) \) |
| 397(1) | \( \delta(\text{F}_{\text{eq}}\text{XeF}_{\text{ax}}) \) | \( \delta(\text{F}_{\text{eq}}\text{AsF}_{\text{eq}}) - \delta(\text{F}_{\text{eq}}\text{AsF}_{\text{eq}}) / \rho_{\text{w}}(\text{F}_{\text{eq}}\text{AsF}_{\text{eq}}) \) |

continued …
Table S6. (continued)

| [F₂Xe(FKrF)₂]AsF₄ | [F₂Xe(FKrF)₂(AsF₆)₂]⁻ |
|------------------|------------------------|
| expt[8,9,c]       | calc[9]                | assign[9]               |
| 380(<1)            | 378(1)[11]            | δ(FeqXeF₆)              |
| 373(2)            | 376(<1)[47]            | δ(FeqAsF₆) - δ(FeqAsF₆) / ρw(FaxAsF₆) |
| 371(2)            | 373(<1)[13]            | δ(FeqAsF₆) - δ(FeqAsF₆) / ρw(FaxAsF₆) |
| 360, sh           | 353(<1)[9]            | δ(FeqAsF₆) + δ(FeqAsF₆) |
|                   | 351(<1)[9]            | δ(FeqAsF₆) + δ(FeqAsF₆) |
| 352(1)            | 342(2)[19]            | δ(FeqAsF₆) - δ(FaxAsF₆) |
| 346(<1), br       | 339(<1)[3]            | δ(FeqAsF₆) + δ(FaxAsF₆) / ρ(FeqAsF₆) |
| 305(2)            | 330(1)[74]            | δ(XeF₄eq)umb            |
| 278(<1)            | 280(1)[15]            | δ(FKrF₆) / [ρ(FeqXeF₆) - ρ(FeqXeF₆)] / ρw(FaxAsF₆)small |
| 273(<1)            | 275(1)[33]            | δ(FKrF₆) / [ρ(FeqXeF₆) - ρ(FeqXeF₆)] / ρw(FaxAsF₆)small |
| 259(<1)            | 266(<1)[3]            | [ρ(FeqXeF₆) - ρ(FeqXeF₆)] |
|                   | 261(1)[11]            | δ(FeqXeF₆) + δ(FeqXeF₆) / δ(FKrF₆)D.p. |
| 251(<1)            | 247(<1)[12]            | δ(FKrF₆)D.p. / [ρw(FeqXeF₆) - ρw(FeqXeF₆)] / ρw(FaxAsF₆)small |
|                   | 246(<1)[11]            | δ(FKrF₆)D.p. / [ρw(FeqXeF₆) - ρw(FeqXeF₆)] / ρw(FaxAsF₆)small |
| 241(<1)            | 239(<0.1)[6]            | [ρw(FeqAsF₆) - ρw(FaxAsF₆)] |
|                   | 237(<1)[9]            | [ρw(FeqAsF₆) - ρw(FaxAsF₆)] |
|                   | 235(<1)[8]            | [ρw(FeqAsF₆) - ρw(FaxAsF₆)] / ρw(FeqXeF₆) |
|                   | 229(<1)[7]            | [δ(FeqXeF₆) - δ(FeqXeF₆)] / [ρw(FeqAsF₆) - ρw(FeqAsF₆)]small |
| 218(<1)[1]            | 213(<0.1)[3]            | [ρw(FeqAsF₆) - ρw(FaxAsF₆)] / ρw(FeqXeF₆) |
| 211(<1)[7]            | 211(<1)[7]            | [δ(FeqXeF₆) - δ(FeqXeF₆)] / [ρw(FeqAsF₆) - ρw(FeqAsF₆)]small |
| 206(<1)[9]            | 150(<1)[3]            | ρ(FaxXeF₄eq) / ρ(FKrF₆)small |
|                   | 140(<1)[5]            | ρ(FaxXeF₄eq) / ρ(FKrF₆) |
| 145(10)            | 136(2)[8]            | ρ(FKrF₆) |
| 110(10)            | 119(2)[1]            | ρ(FKrF₆) |

continued ...
Table S6. (continued)

| [F₅Xe(FKrF)₂AsF₆]⁻ | [F₅Xe(FKrF)₂(AsF₆)₂]⁻ |
|---------------------|-----------------------|
| expt[a,b,c]         | calcd[d]              | assgnts[e]  |
| 115(3)[1]           | ρ(AsF₆)               |             |
| 92(2)[9]            | ρ(F,KrF₆)             |             |
| 108(1)[14]          |                       | deformation modes |
| 103(<1)[8]          |                       |               |
| 94(1)[4]            |                       |               |
| 83(<1)[4]           |                       |               |
| 76(<1)[1]           |                       |               |
| 66(1)<1             |                       |               |
| 61(1)<1             |                       |               |
| 56(<1)<1            |                       |               |
| 51(1)<1             |                       |               |
| 45(<1)<1            |                       |               |
| 41(<1)<1            |                       |               |
| 34(<1)<1            |                       |               |
| 34(1)<1             |                       |               |
| 31(1)<1             |                       |               |
| 16(1)[1]            |                       |               |
| 13(1)<1             |                       |               |
| 139, sh             |                       | lattice modes  |
| 133, sh             |                       |               |
| 95, vbr             |                       |               |

[a] Frequencies are given in cm⁻¹.

[b] Values in parentheses denote relative Raman intensities. Abbreviations denote shoulder (sh), broad (br), and very broad (vbr). The Raman spectrum was recorded in a FEP sample tube at −161 °C using 1064-nm excitation (Figure 3).

[c] The bands observed at 719(sh), 693(sh), 675(20), 650(sh), 608(sh), 590(3), 549(19), 540(sh), 454(22), 411(2), 407(sh), 368(2), 344(<1), 249(<1), 268(<1), and 130(sh) cm⁻¹ are assigned to [F₅Xe(FKrF)AsF₆].

[d] Values in parentheses and square brackets denote calculated Raman intensities (Å⁴ amu⁻¹) and infrared intensities (km mol⁻¹), respectively.

[e] Assignments are for the energy-minimized geometry (C₁) calculated using the APFD/aVDZ(-PP)(Xe, As, Kr)/aVDZ(F) level of theory. Abbreviations denote stretch (ν), bend (δ), rock (ρ), twist (ρₜ), and wag (ρₔ), umbrella (umb), equatorial (eq), axial (ax), F bridging on the AsF₆ group (Fᵦₐ), F cis to an Fᵦₐ atom (Fᵦₛ), F trans to an Fᵦₐ atom (Fₜₐ), in-plane (i.p.), and out-of-plane (o.o.p.). Bond elongations and angle openings are denoted by plus (+) signs, and bond contractions and angle compressions are denoted by minus (−) signs. The in-plane and out-of-plane bending modes are relative to the XeF₅,KrF₆-plane, where the atom labeling scheme corresponds to that used in Figure 1b.

[f] The band overlaps with another [F₅Xe(FKrF)₂AsF₆] band.
Table S7. Experimental and calculated vibrational frequencies[a] and intensities for KrF$_2$

|        | exptl   | calcd[b]  | assgn[c]   |
|--------|---------|-----------|------------|
| ν$_3$(∑u') | 588[d]  | 612(0)[265] | ν$_3$(KrF$_2$) |
| ν$_1$(∑g')  | 465.5[e] | 514(53)[0]  | ν$_4$(KrF$_2$) |
| ν$_2$ (∏u)  | 469.5, 468.6[f] | 239(0)[13]  | δ(KrF$_2$)      |

[a] Frequencies are given in cm$^{-1}$.  
[b] The APFD/aVDZ(-PP)(Kr)/aVDZ(F) level of theory was used. The calculated Kr−F bond length was 1.889 Å. Values in parentheses and square brackets denote calculated Raman intensities (Å$^4$ amu$^{-1}$) and infrared intensities (km mol$^{-1}$), respectively.  
[c] Abbreviations denote symmetric (s), asymmetric (as), stretch (ν) and bend (δ).  
[d] Infrared frequencies were obtained from KrF$_2$ vapor; ref [S6].  
[e] The frequency of ν$_1$(∑g') of α-KrF$_2$ (−196 °C) was obtained from the Raman spectrum; ref [S7].  
[f] Raman frequencies are for β-KrF$_2$ (−80 °C); ref [S8].

Table S8. Calculated vibrational frequencies[a] and intensities for [XeF$_5$]$^+$ and IF$_5$

| [XeF$_5$]$^+$[b,d] | IF$_5$ [b,d,e] | assgn[f]   |
|---------------------|----------------|------------|
| 713 (<1)[152]       | 640 (<1)[257]  | ν(MF$_1$) − ν(MF$_3$) |
| 674 (15)[21]        | 683 (19)[50]   | ν(MF$_{ax}$) |
| 635 (28)[2]         | 603 (22)[1]    | ν(MF$_{4eq}$) − ν(MF$_{ax}$)$_{small}$ |
| 624 (16)[0]         | 581 (16)[0]    | [ν(MF$_1$) + ν(MF$_3$)] − [ν(MF$_2$) + ν(MF$_4$)] |
| 332 (2)[8]          | 326 (1)[9]     | δ(F$_1$MF$_{ax}$) − δ(F$_3$MF$_{ax}$) |
| 301 (1)[31]         | 284 (1)[38]    | δ(MF$_{4eq}$)$_{umb}$ |
| 257 (3)[0]          | 241 (2)[0]     | δ(F$_1$MF$_2$) + δ(F$_3$MF$_4$) |
| 196 (<0.1)[0]       | 183 (<0.1)[0]  | [ρ$_w$(F$_1$MF$_3$) − ρ$_w$(F$_2$MF$_4$)] |
| 192 (1)[3]          | 173 (<1)[3]    | δ(F$_1$MF$_3$) |

[a] Frequencies are given in cm$^{-1}$.  
[b] The APFD/aVDZ(-PP)(Kr)/aVDZ(F) level of theory was used.  
[c] Calculated geometrical parameters: d(Xe−F$_{ax}$) = 1.864 Å, d(Xe−F$_{eq}$) = 1.887 Å, ∠(F$_{ax}$XeF$_{eq}$) = 83.3°, ∠(F$_{eq}$XeF$_{ax}$) = 89.2° and 166.7°.  
[d] Calculated geometrical parameters: d(I−F$_{ax}$) = 1.872 Å, d(I−F$_{eq}$) = 1.928 Å, ∠(F$_{ax}$IF$_{eq}$) = 82.9°, ∠(F$_{eq}$IF$_{ax}$) = 89.1° and 165.7°.  
[e] Values in parentheses and square brackets denote calculated Raman intensities (Å$^4$ amu$^{-1}$) and infrared intensities (km mol$^{-1}$), respectively.  
[f] Abbreviations denote symmetric (s), asymmetric (as), stretch (ν), and bend (δ).
Figure S10. Calculated geometry [APFD/aVDZ(-PP)(Kr, Xe, As)/aVDZ(F)] of [F$_5$Xe(FKrF)AsF$_6$] (1$^*$$^*$).
Figure S11. Calculated geometries $[\text{APFD/aVDZ(-PP)(Kr, Xe, As)/aVDZ(F)}]$ of a) $[\text{FsXe(FKrF)(AsF}6\text{)}]^{2-}$ (1') and b) $[\text{FsXe(FKrF)}]_{2}(\text{AsF}6\text{)}]^{-}$ (2').
Table S9. Natural population analysis (NPA) charges, Wiberg valences, and Wiberg bond indices for 
[F_{5}Xe(FKrF)(AsF_{6})]^{2−} (1'), [F_{5}Xe(FKrF)AsF_{6}] (1''), [F_{5}Xe(FKrF)_{2}(AsF_{6})]^{−} (2'), [XeF_{5}]^{+}, IF_{5}, and KrF_{2}[a]

| Bond Indices | NPA Charges [Valences] | Bond Indices | NPA Charges [Valences] |
|--------------|------------------------|--------------|------------------------|
| Xe−F1       | 0.550                  | Xe−F1       | 0.594                  |
| Xe−F2       | 0.596                  | F1          | −0.490 [0.817]         |
| Xe−F3       | 0.595                  | F2          | −0.485 [0.848]         |
| Xe−F4       | 0.601                  | F3          | −0.485 [0.847]         |
| Xe−F5       | 0.600                  | F4          | −0.480 [0.855]         |
| F5          | −0.481 [0.854]         | Xe−F5       | 0.600                  |
| Kr1−F12     | 0.610                  | Kr1         | 1.058                  |
| Kr1−F13     | 0.450                  | F12         | −0.453 [0.809]         |
| F13         | −0.513 [0.820]         | KrF_{2}     | 0.092                  |
| As−F6       | 0.550                  | As          | 2.787 [3.099]          |
| As−F7       | 0.542                  | F6          | −0.604 [0.690]         |
| As−F8       | 0.531                  | F7          | −0.610 [0.682]         |
| As−F9       | 0.529                  | F8          | −0.619 [0.667]         |
| As−F10      | 0.553                  | F9          | −0.624 [0.659]         |
| As−F11      | 0.386                  | F10         | −0.603 [0.693]         |
| F11         | −0.645 [0.663]         | As_{i}−F6  | 0.529                  |
| As_{i}−F7  | 0.527                  | F6_{i}      | −0.621 [0.665]         |
| As_{i}−F8  | 0.518                  | F7_{i}      | −0.623 [0.660]         |
| As_{i}−F9  | 0.466                  | F8_{i}      | −0.630 [0.652]         |
| As_{i}−F10 | 0.538                  | F9_{i}      | −0.646 [0.642]         |
| As_{i}−F11 | 0.521                  | F10_{i}     | −0.615 [0.673]         |
| F11_{i}     | −0.628 [0.651]         | As_{ii}−F6| 0.521                  |
| As_{ii}−F7 | 0.527                  | F6_{ii}     | −0.628 [0.651]         |
| As_{ii}−F8 | 0.518                  | F7_{ii}     | −0.623 [0.661]         |
| As_{ii}−F9 | 0.529                  | F8_{ii}     | −0.630 [0.653]         |
| As_{ii}−F10| 0.463                  | F9_{ii}     | −0.621 [0.665]         |
| As_{ii}−F11| 0.540                  | F10_{ii}    | −0.646 [0.645]         |
| F11_{ii}    | −0.613 [0.675]         | As_{iii}−F6| 0.512                  |
| As_{iii}−F7| 0.527                  | F6_{iii}    | −0.628 [0.651]         |
| As_{iii}−F8| 0.518                  | F7_{iii}    | −0.623 [0.661]         |
| As_{iii}−F9| 0.529                  | F8_{iii}    | −0.630 [0.653]         |
| As_{iii}−F10| 0.463                  | F9_{iii}    | −0.621 [0.665]         |
| As_{iii}−F11| 0.540                  | F10_{iii}   | −0.646 [0.645]         |
| F11_{iii}   | −0.613 [0.675]         | As_{iv}−F6 | 0.512                  |
| As_{iv}−F7 | 0.527                  | F6_{iv}     | −0.628 [0.651]         |
| As_{iv}−F8 | 0.518                  | F7_{iv}     | −0.623 [0.661]         |
| As_{iv}−F9 | 0.529                  | F8_{iv}     | −0.630 [0.653]         |
| As_{iv}−F10| 0.463                  | F9_{iv}     | −0.621 [0.665]         |
| As_{iv}−F11| 0.540                  | F10_{iv}    | −0.646 [0.645]         |
| F11_{iv}    | −0.613 [0.675]         | \sum_{As_{i}F_{6}}= & −0.918 \sum_{As_{ii}F_{6}}= & −0.978 \sum_{As_{iii}F_{6}}= & −0.978 \sum_{As_{iv}F_{6}}= & −0.978 
| Xe−F13(Kr)  | 0.102                  | Xe−F13(Kr)  | 0.070                  |
| Xe−F9(As_{i}) | 0.028              | Xe−F11(As_{i}) | 0.104               |
| Xe−F10(As_{ii}) | 0.031             | Xe−F6(As_{ii}) | 0.097               |
| Xe−F11(As_{iii}) | 0.098             |

continued ...
Table S9. (continued)

| Bond Indices | NPA Charges [Valences] | Bond Indices | NPA Charges [Valences] |
|--------------|------------------------|--------------|------------------------|
| Xe−F1 0.566  | Xe 3.191 [3.226]       | Xe−F1 0.647  | Xe 3.173 [3.228]       |
| Xe−F2 0.595  | F1 −0.475 [0.835]      | Xe−F2 0.645  | F1 −0.384 [0.943]      |
| Xe−F3 0.607  | F2 −0.484 [0.848]      | Xe−F3 0.645  | F2 −0.447 [0.898]      |
| Xe−F4 0.598  | F3 −0.473 [0.861]      | Xe−F4 0.645  | F3 −0.447 [0.898]      |
| Xe−F5 0.597  | F4 −0.481 [0.853]      | Xe−F5 0.645  | F4 −0.447 [0.898]      |
| F5 −0.507 [0.819] |        | F5 −0.447 [0.898] |        |

∑_{XeF5}^{+} 0.771

| Bond Indices | NPA Charges [Valences] | Bond Indices | NPA Charges [Valences] |
|--------------|------------------------|--------------|------------------------|
| Kr1−F12 0.603 | Kr1 1.043 [1.091]      | I−F1 0.609   | I 2.901 [2.855]        |
| Kr1−F13 0.464 | F12 −0.456 [0.807]    | I−F2 0.562   | F1 −0.531 [0.789]      |
|              | F13 −0.526 [0.783]    | I−F3 0.562   | F2 −0.592 [0.707]      |
|              | ∑_{KrF2}^{+} 0.061    | I−F4 0.562   | F3 −0.592 [0.707]      |
| Kr2−F14 0.576 | Kr2 1.020 [1.097]      | I−F5 0.562   | F4 −0.592 [0.707]      |
| Kr2−F15 0.502 | F14 −0.475 [0.789]    | F5 −0.592 [0.707] |        |
|              | F15 −0.514 [0.779]    | ∑_{IF5}^{+} 0.000 |
|              | ∑_{KrF2}^{+} 0.031    |              |
| As−F6 0.542  | As 2.785 [3.103]       | Kr−F 0.551   | Kr 0.984 [1.102]        |
| As−F7 0.534  | F6 −0.611 [0.680]      | Kr−F 0.551   | F −0.492 [0.772]        |
| As−F8 0.551  | F7 −0.617 [0.673]      |              |
| As−F9 0.537  | F8 −0.604 [0.690]      |              |
| As−F10 0.549 | F9 −0.613 [0.679]      |              |
| As−F11 0.382 | F10 −0.609 [0.683]     |              |
|              | F11 −0.647 [0.659]     |              |
|              | ∑ −0.916               |              |
| As^{+}−F6^{+} | As^{+} 2.786 [3.103]   |              |
| As^{+}−F7^{+} | F6^{+} −0.607 [0.686]  |              |
| As^{+}−F8^{+} | F7^{+} −0.618 [0.673]  |              |
| As^{+}−F9^{+} | F8^{+} −0.620 [0.668]  |              |
| As^{+}−F10^{+} | F9^{+} −0.618 [0.672]  |              |
| As^{+}−F11^{+} | F10^{+} −0.663 [0.632] |              |
|              | F11^{+} −0.607 [0.686] |              |
|              | ∑ −0.947               |              |
|              | ∑_{AsF6}^{−} −1.864    |              |

Xe---F13(Kr) 0.069
Xe---F15(Kr) 0.037
Xe---F11(As) 0.096
Xe---F10(As) 0.068

[a] APFD/aVDZ(-PP)(Kr, Xe, As)/aVDZ(F).
Figure S12. ELF isosurface plots (APFD/aVDZ(-PP)(Kr, Xe, As)/aVDZ(F), \(\eta(r) = 0.55\)) for \([\text{XeF}_5]^+\), IF\(_5\), and KrF\(_2\). Color code: red = core basin; C(Ng), C(I); blue = monosynaptic valence basin; V(F), V(Ng), V(I).
Experimental Section

**Caution!**
Anhydrous HF must be handled using appropriate protective gear with easy access to proper treatment procedures in the event of contact with the liquid, vapor or its solutions. Xenon hexafluoride, [XeF$_6$]$^-$ salts, and KrF$_2$ are potent oxidative fluorinators and highly energetic materials that are only stable under the rigorously anhydrous conditions employed in the experimental procedures outlined in this paper. Xenon hexafluoride, KrF$_2$, and [XeF$_6$]$^-$ salts can potentially detonate upon hydrolysis or contact with organic materials. Hydrolysis of XeF$_6$ and [XeF$_5$]$^-$ salts forms highly toxic HF and XeO$_3$, a highly endothermic, shock-sensitive detonator when isolated as a dry solid. It is therefore imperative that the syntheses of the aforementioned compounds be restricted to small quantities (<100 mg) and that their syntheses and other manipulations be carried out in FEP (perfluoroethylene/perfluoropropylene copolymer) vessels to avoid sharp fragments in the event of a detonation. The use of adequate protective apparel and shielding are crucial for the safe handling of the aforementioned compounds. Utmost precautions must be taken when disposing of these compounds and their derivatives.

**Apparatus**
Manipulations involving air-sensitive compounds were carried out under anhydrous conditions on glass and metal (316 stainless steel and nickel) high-vacuum lines and in the inert atmosphere of a dry box as previously described. Syntheses were carried out in cylindrical reaction vessels fabricated from ¼-in. o.d. (⅛-in. wall thickness) lengths of FEP (perfluoroethylene/perfluoropropylene copolymer) tubing. The tubing was heat-sealed at one end, heat flared at the other end, and connected through a 45° SAE flare nut to the conical end of a Kel-F (chlorotrifluoroethylene polymer) valve to form a compression seal. Modified, T-shaped reaction vessels were fabricated by fusing a length of FEP tubing at right angles to the original length of tubing and heat-sealing its open end. Reaction vessels and sample tubes were rigorously dried under dynamic vacuum prior to passivation at ca. 1 atm of F$_2$ gas for several hours. Vacuum line connections were made by use of ¼-in. 316 stainless steel Swagelok Ultra-Torr unions fitted with Viton O-rings.

**Starting Materials**
Technical grade fluorine gas (Air Products, 98% pure) and nitrogen gas (Praxair, 99.995%, H$_2$O < 0.5 ppm) were used without further purification. Fluorine was dispensed as previously described through the dry, fluorine-passivated manifold of a metal vacuum line.

Anhydrous HF (Harshaw Chemicals Co.) was purified as previously described and stored in a Kel-F container equipped with a Kel-F valve. Small quantities of aHF (ca. 0.1–0.5 mL) were transferred under static vacuum through a dry, fluorine-passivated FEP submanifold attached to a metal vacuum line.

Krypton difluoride was prepared by use of a hot-wire reactor and purified as previously described and stored in an FEP vessel at −78 °C in solid dry ice.

Xenon hexafluoride was synthesized by heating Xe with F$_2$ in a 1:24 molar ratio under autogenous pressure in a 300-mL nickel vessel to a temperature of 280 °C as previously described. Small amounts of XeOF$_4$ and HF, which likely formed by the reaction of XeF$_6$ with trace amounts of moisture or metal oxide on the reaction vessel surfaces, were removed by flash distillation under dynamic vacuum at room temperature. Xenon hexafluoride contained a small amount of XeF$_4$ impurity (<1%), which was converted to XeF$_6$ by the addition of KrF$_2$ and melting the bulk solid by slow heating, with constant agitation, to 45 °C.

Anhydrous HF (aHF), XeF$_6$, and KrF$_2$ were transferred under static vacuum through ¼-in. o.d. × ⅛-in. i.d. FEP submanifolds connected to a metal vacuum line.

The salt, [XeF$_6$][AsF$_6$], was synthesized in a ¼-in. o.d. × ⅛-in i.d. FEP reaction tube by reaction of XeF$_6$ and AsF$_5$ in aHF as previously described. After removal of excess AsF$_6$ and aHF solvent under dynamic vacuum, the resulting white powder was stored inside a dry box in the FEP reaction vessel used for its synthesis.
Syntheses and Crystal Growth

**[FsXe(FKrF)AsF₆]** (1) and **[FsXe(FH)AsF₆]** (3). Xenon hexafluoride (32.9 mg, 0.134 mmol, 1.00 equiv.) was sublimed under static vacuum into the main arm of a T-shaped reactor that had been cooled to −196 °C. Anhydrous HF (~0.30 mL) was condensed under static vacuum onto XeF₆ at −196 °C and was followed by condensation of gaseous AsF₅ (~1.4 equiv.) onto the frozen XeF₆/HF mixture at −196 °C. Warming the mixture to −78 °C gave a colorless solution which, upon slow removal of aHF and unreacted AsF₅ at −78 °C, yielded colorless needle-shaped crystals of [FsXe(FH)AsF₆] (see below). The Raman spectrum of [FsXe(FH)AsF₆] was recorded at −150 °C prior to redissolution in aHF (0.16 mL). Krypton difluoride (24.9 mg, 0.204 mmol, 1.52 equiv.) was sublimed into the vessel and the solution volume was then reduced to half by removal of aHF under dynamic vacuum at −78 °C. Cooling the solution to −90 °C and removal of aHF solvent under dynamic vacuum yielded colorless crystals of [FsXe(FKrF)AsF₆]. The LT (−144 °C) Raman spectrum of the crystalline product was recorded in the FEP reaction vessel (Figure 3a) and a single crystal of 1 was selected and mounted for a LT SCXRD structure determination.

**[FsXe(FKrF)₂AsF₆]** (2). Xenon hexafluoride (9.4 mg; 0.038 mmol, 1.00 equiv.) was condensed at −78 °C into a T-shaped FEP reaction vessel followed by condensation of aHF (0.11 mL) and a stoichiometric excess of AsF₅ (~1.9 equiv.) at −196 °C. The mixture was warmed to −78 °C to effect dissolution. Removal of unreacted AsF₅ and HF at −78 °C resulted in a white powder. The sample was redissolved in aHF (0.02–0.04 mL) and excess of KrF₂ (16.3 mg, 0.134 mmol, 3.52 equiv.) was condensed into the vessel at −196 °C. Warming of the reaction mixture to −30 °C resulted in a clear solution that was slowly cooled to −75 °C over a period of 7 h. Slow removal of aHF under dynamic vacuum at −75 °C yielded a finely divided white solid and colorless crystals of [FsXe(FKrF)₂AsF₆] that were suitable for a SCXRD determination. The Kr–F stretching region in the LT (−148 °C) Raman spectrum of the crystalline sample was dominated by an intense ν₅(KrF₂) stretching band due to excess KrF₂.

A sample that was free of uncoordinated KrF₂ was also prepared by reaction of [XeF₅][AsF₆] (19.37 mg, 0.04665 mmol, 1.00 equiv.) and KrF₂ (11.8 mg, 0.097 mmol, 2.08 equiv.) in aHF (0.20 mL of solution) using a similar synthetic procedure. The solvent was removed under dynamic vacuum at −78 °C and the resulting white solid was used to obtain a LT (−161 °C) Raman spectrum, which showed the sample was mainly comprised of [FsXe(FKrF)₂AsF₆] with a small amount of [FsXe(FKrF)AsF₆] (Figure 3b).

**Attempted Synthesis of [(FsXe)₂(μ-FKrF)(AsF₆)]** and **Synthesis of [FsXe(FH)AsF₆]** (3). Krypton difluoride (6.66 mg, 0.055 mmol, 1.00 equiv.) was sublimed into a T-shaped FEP reaction vessel at −196 °C under static vacuum. The reaction vessel was then transferred into a N₂-filled glovebox through a cold port and maintained below −100 °C in a cryowell while [XeF₅][AsF₆] (44.64 mg, 0.1075 mmol, 1.95 equiv.) was added to the reaction vessel. Anhydrous HF was condensed under static vacuum onto the sample mixture at −196 °C. The reagents dissolved to give a clear, colorless solution (~0.36 mL) upon warming to −78 °C. The sample volume was reduced to ~0.09 mL by removal of the solvent under dynamic vacuum at −78 °C.

The reaction mixture was warmed to −36 °C and the clear colorless solution was slowly cooled to −81 °C over a period of 6 h to afford crystals of [FsXe(FKrF)AsF₆] and [FsXe(FH)AsF₆], as shown by LT single-crystal X-ray diffraction (SCXRD) determination and LT Raman spectroscopy. Anhydrous HF solvent was removed under dynamic vacuum at −78 °C, and the reaction vessel was backfilled with 1000 Torr of dry N₂ and stored at −78 °C. A single crystal of 3 was selected and mounted for a LT SCXRD determination.

**Synthesis and Crystallization of [FsXe(FH)SbF₆]** (4). An attempt to coordinate KrF₂ to the [XeOF₃]⁺ cation by crystallization of an aHF solution containing a mixture of [XeOF₃][SbF₆] and KrF₂ at −80 °C resulted in crystalline [FsXe(FH)SbF₆] and the known cocrystal, [XeF₅][SbF₆]·XeOF₃, which was verified by Raman spectroscopy[617] and a unit cell determination.[618]

A T-shaped reaction vessel was loaded with SbF₆ (19.45 mg, 0.1088 mmol, 1.00 equiv.) inside a dry box and aHF (~0.14 mL) was condensed into the reaction vessel at −196 °C and ca.1000 Torr of F₂ gas was added to the reaction vessel at −78 °C. The reaction vessel valve was closed and the reactor and contents were warmed to room temperature and periodically agitated, whereupon all SbF₆ dissolved within ca. 30 min to give a clear, colorless solution of SbF₆. Xenon oxide tetrafluoride (36.0 mg, 0.161 mmol, 1.48 equiv.) was condensed under static vacuum onto the frozen solution at −196 °C. Warming to room temperature resulted in a solution of [XeOF₃][SbF₆] and excess XeOF₃ (0.48 equiv.). Krypton difluoride (20.1 mg, 0.165 mmol,
1.51 equiv.) was then condensed into the reactor under static vacuum at −196 °C. A clear yellow solution was obtained when the reaction mixture was warmed to −30 °C and a pale yellow crystalline precipitate formed upon cooling to −78 °C. The reaction mixture was rewarmed to −30 °C, whereupon most of the solid dissolved. Slow cooling of the solution to −80 °C over a period of 6.5 h yielded colorless crystals of 

\[ \text{[F}_5\text{Xe}(\text{FH})\text{SbF}_6] \] that were suitable for a SCXRD determination. Crystals were isolated by removal of aHF solvent under dynamic vacuum at −80 °C to −78 °C. The reaction vessel was backfilled with ca. 1000 Torr of dry N\(_2\) and stored at −78 °C. A single crystal of 4 was selected and mounted for a LT SCXRD determination.

The Raman spectrum of the crystalline material, recorded at −127 °C, showed bands assigned to 

\[ \text{[XeOF}_3\text{][SbF}_6] \] small amounts of KrF\(_2\), [O\(_2\)][SbF\(_6\)]\(_2\) and an unidentified compound whose bands are tentatively assigned to [F\(_5\)Xe(FH)SbF\(_6\)] (Figure S13). The proposed reaction pathway is given by Equations (5–9) and is consistent with the previously reported reaction of XeOF\(_4\) with [KrF][SbF\(_6\)] which yields [XeF\(_5\)][SbF\(_6\)]-XeOF\(_4\)\([S17\)]

\[
\begin{align*}
[XeOF_3][SbF_6] + KrF_2 & \rightarrow [KrF][SbF_6] + XeOF_4 & (5) \\
XeOF_4 + [KrF][SbF_6] & \rightarrow [XeF_5][SbF_6] + \frac{1}{2} O_2 + Kr & (6) \\
[KrF][SbF_6] + O_2 & \rightarrow [O_2][SbF_6] + Kr + \frac{1}{2} F_2 & (7) \\
[XeF_5][SbF_6] + HF & \rightarrow [F_5Xe(FH)SbF_6] & (8) \\
[XeF_5][SbF_6] + XeOF_4 & \rightarrow [XeF_5][SbF_6]-XeOF_4 & (9)
\end{align*}
\]

Single-Crystal X-ray Diffraction

Crystal Mounting Procedure
Crystalline samples were stored in their respective FEP reaction vessels under a dry nitrogen or argon at −78 °C until a suitable crystal could be selected and mounted on the diffractometer using a previously described LT crystal mounting procedure.\([S20\)] Crystals were rapidly dumped from the reaction vessel into an aluminum trough which had been cooled to −70 to −90 ±5 °C by means of a cold stream of dry N\(_2\) gas. The cold trough allowed individual crystals to be selected under a stereomicroscope while protected by the cold aluminum trough which had been cooled to −196 °C in liquid N\(_2\). The selected crystal was attached at the tip of a dual-thickness polymer loop (MiTeGen, Ithaca, NY; MicroLoops™ 100–500 μm) using perfluoropolyether oil (Fomblin Z-25) as the adhesive. The loop was mounted on the diffractometer using a previously described LT crystal mounting procedure.\([S19\)]

Collection and Reduction of X-ray Data
Crystals were centered on a Bruker SMART APEX II diffractometer equipped with an APEX II 4K CCD (charge-coupled device) area detector and a fixed-\(\chi\) triple-axis goniometer that was controlled by the APEX2 Graphical User Interface (GUI) software.\([S21\)] A Bruker Triumph curved crystal monochromator was used with a Mo Ka (\(\lambda = 0.71073 \) Å) radiation source. Diffraction data was collected in a 512 × 512 pixel mode using 2 × 2 pixel binning, with \(\omega\)-scans and \(\phi\)-scans at 0.5° intervals (\(\omega\), 12 × 404; \(\phi\), 1 × 720 for (1); \(\omega\), 6 × 404, 3 × 408; \(\phi\), 1 × 720 for (2); \(\omega\), 9 × 202, 3 × 204; \(\phi\), 1 × 360 for (3); \(\omega\), 11 × 404, 5 × 408; \(\phi\), 2 × 720 for (4)). The crystal-to-detector distance was 4.955 cm. Also see Table S10 for additional parameters.

Solution and Refinement of the Structure
Data integration was performed using SAINT\([S22\)] within the APEX2 GUI software.\([S21\)] The scaling of the diffraction data and a multi-scan absorption correction were completed with the SADABS program.\([S23\)] XPREP\([S24\)] was used to analyze the symmetry of the data and determine the space group.\([S24\)] The crystal structures were solved with SHELXT\([S25\)] and refined with SHELXL\([S26\)] programs, within the Olex2 software.\([S27\)] The final refinement was obtained by introducing anisotropic thermal parameters and the recommended weightings. The hydrogen atom in (3) was placed at a location derived from a difference map and refined with a distance restraint (DFIX) of 0.95 Å with a sigma value of 0.02 Å and with \(U_{iso}\) fixed at 1.2 times of the parent fluorine atom. The highest peak and
deepest hole in the final difference Fourier map were typically located in the vicinity of xenon atoms. The crystal structure of [F\textsubscript{5}Xe(AsF\textsubscript{5})] was twinned (HKLF5 refinement, BASF 0.198), its unit cell was determined by Cell._Now\textsuperscript{[S28]} and the data were treated by TWINABS.\textsuperscript{[S29]} Molecular graphics were created using the DIAMOND program.\textsuperscript{[S30]}

**Raman Spectroscopy**

The Raman spectrum was recorded on a Bruker RFS 100 FT-Raman spectrometer using 1064-nm excitation, 300 mW laser power, and ±0.5 cm\textsuperscript{-1} resolution for samples contained in ¼-in. o.d. × 1/32-in. wall thickness FEP vessels. Low-temperature samples were cooled inside a Pyrex tube that was surrounded by a concentric unsilvered Dewar and mounted inside the macrochamber of the Raman spectrometer. Samples were inserted into the Dewar and cooled by passing a cold stream of N\textsubscript{2} gas through the tube. The N\textsubscript{2} cold stream was produced and regulated by resistively heating liquid N\textsubscript{2} by use of a Bruker R 495 low-temperature accessory.

**Computational Details**

Quantum-chemical calculations were used to assess the bonding in [F\textsubscript{5}XeFKrF](AsF\textsubscript{6})\textsuperscript{3−} (1') (C), [F\textsubscript{2}XeFKrF]\textsuperscript{2−} (1") (C), [F\textsubscript{5}XeFKrF]2(AsF\textsubscript{6})\textsuperscript{2−} (2') (C), [XeF\textsubscript{5}]\textsuperscript{+} (C\textsubscript{4v}), and KrF\textsubscript{2} (D\textsubscript{∞h}). The DFT functionals, B3LYP, PBE1PBE, and APFD, which includes dispersion, were employed using the aug-cc-pVDZ(-PP), aug-cc-pVTZ(-PP), and/or Def2-TZVPD, basis sets. Although all calculations resulted in stationary points with all frequencies real, the APFD/aug-cc-pVDZ(-PP) level gave the best agreement with experiment and was therefore used for the paper. The basis sets were obtained from the EMSL Basis Set Library through the Basis Set Exchange.\textsuperscript{[S31]} The Gaussian 09 software\textsuperscript{[S32]} was used for geometry optimizations and vibrational frequencies and intensities calculations. The vibrational displacements that form the basis for the vibrational mode descriptions in Tables S5, S6, and S8 were visualized by the GaussView program.\textsuperscript{[S33]} Natural bond orbital (NBO) analyses were carried out employing NBO 6.0 program.\textsuperscript{[S34]} AIM and ELF analyses were carried out by use of the Multiwfn package\textsuperscript{[S35]} and the formatted G09 wavefunction files as input. In addition, ELF basins were also analyzed by using the program UCSF Chimera.\textsuperscript{[S36]} The MEPS contours were drawn using the GaussView program.\textsuperscript{[S33]}
Figure S13. The Raman spectrum was obtained from the reaction of \([\text{XeOF}_3][\text{SbF}_6]\) with \(\text{KrF}_2\) in the presence of 0.48 equiv. of \(\text{XeOF}_4\). The spectrum was recorded in a FEP sample tube at \(-127 \, ^\circ\text{C}\) using 1064-nm excitation and mainly consists of bands due to \([\text{XeF}_5][\text{SbF}_6]\cdot\text{XeOF}_4\), which are indicated by bullets (•) \((920(21), 695(44), 675(7), 652(10), 615(100), 574(65), 560(12), 540(67), 408(6), 371(9), 360(2), 312(5), 294(5), 282(4), 277(3), 234(6), 161(1) \, \text{cm}^{-1})\). The spectrum also shows a small amount of \(\text{KrF}_2\) (§) at 463(12) cm\(^{-1}\) and a trace amount of \([\text{O}_2][\text{SbF}_6]\) at 1863(0.5) cm\(^{-1}\) (\(\nu(\text{OO})\), not shown). Bands arising from a small amount of an unidentified compound are also present \((664(\text{sh}), 661(\text{sh}), 658(10), 635(6), 632(\text{sh}), 622(\text{sh}), 583(\text{sh}), 553(1), 507(1), 503(3), 417(1), 137(1), 128(1) \, \text{cm}^{-1})\) which are tentatively assigned to \([\text{F}_3\text{Xe(FH)SbF}_6]\). Other symbols denote FEP sample tube bands (*) and an instrumental artifact (†).
Table S10. Summary of Crystal Data and Structure Refinements for [F₅Xe(KrF)AsF₆] (1), [F₅Xe(KrF)₂AsF₆] (2), [F₅Xe(H)AsF₆] (3), and [F₅Xe(H)SbF₆] (4)

| Compound | [F₅Xe(KrF)AsF₆] | [F₅Xe(KrF)₂AsF₆] | [XeF₅(H)AsF₆] | [XeF₅(H)SbF₆] |
|----------|-----------------|-----------------|---------------|---------------|
| Formula  | AsF₅KrXe       | AsF₅Kr₂Xe       | F₁₂HAsXe      | F₁₂HSbXe      |
| Fw       | 537.02          | 658.82          | 435.23        | 482.06        |
| T (K)    | 100             | 100             | 100           | 100           |
| Crystal system | monoclinic    | monoclinic     | monoclinic   | monoclinic   |
| Space group | P2₁/n         | P2₁/c          | P2₁/c        | P2₁/c        |
| a (Å)    | 9.03170(10)    | 9.3142(5)       | 12.2989(4)    | 12.2989(4)    |
| b (Å)    | 9.7065(2)       | 8.0482(4)       | 10.6717(3)    | 6.3279(2)     |
| c (Å)    | 12.1261(2)      | 16.1545(8)      | 90            | 15.2663(4)    |
| α (°)    | 90              | 90              | 90            | 90            |
| β (°)    | 106.8920(10)   | 95.942(3)       | 106.3167(19)  | 90            |
| γ (°)    | 90              | 90              | 90            | 90            |
| V (Å³)   | 1017.18(3)      | 1204.48(11)     | 816.91(4)     | 851.45(4)     |
| Z        | 4               | 4               | 4             | 4             |
| Dcalcd (g cm⁻³) | 3.507   | 3.633           | 3.539         | 3.761         |
| Crystal size (mm) | 0.44 × 0.30 × 0.15 | 0.17 × 0.14 × 0.11 | 0.20 × 0.12 × 0.07 | 0.36 × 0.29 × 0.24 |
| Radiation type | Mo Kα       | Mo Kα          | Mo Kα        | Mo Kα        |
| λ (Å)    | 0.71073         | 0.71073         | 0.71073       | 0.71073       |
| μ (mm⁻¹) | 11.101          | 13.062          | 8.411         | 7.319         |
| F(000)   | 960             | 1176            | 784           | 856           |
| θmax (°) | 47.762          | 40.276          | 34.261        | 44.243        |
| Index ranges | −18 ≤ h ≤ 18 | −16 ≤ h ≤ 16 | −19 ≤ h ≤ 18 | −12 ≤ h ≤ 12 |
|            | −20 ≤ k ≤ 20   | −14 ≤ k ≤ 14   | 0 ≤ k ≤ 10   | −29 ≤ k ≤ 29 |
|            | −25 ≤ l ≤ 25   | −29 ≤ l ≤ 28   | 0 ≤ l ≤ 16   | −17 ≤ l ≤ 17 |
| Reflections collected | 101662 | 63042          | 93344 [d]    | 105078        |
| Independent refns. | 9617    | 7573            | 3461          | 6722          |
| Reflns. with | 7694     | 5541            | 3177          | 6124          |
| Rint     | 0.0499        | 0.0654          | 0.0708 [d]   | 0.0298        |
| Rsigma   | 0.0229        | 0.0414          | 0.0377        | 0.0138        |
| Data/restraints/param. | 9617/0/146 | 7573/0/173     | 3461/0/135   | 6722/1/131    |
| S [b]    | 1.090         | 1.008           | 1.068         | 1.205         |
| R₁ [b]   | 0.0288, 0.0517 | 0.0306, 0.0510 | 0.0228, 0.0413 | 0.0195, 0.0408 |
| R₁ [b]   | 0.0450, 0.0561 | 0.0577, 0.0568 | 0.0294, 0.0452 | 0.0239, 0.0415 |
| Δρmin, Δρmax (eÅ⁻³) | −2.657, 1.879 | −1.164, 1.142  | −0.898, 1.742 | −1.188, 1.411 |

[a] S = [Σ(w(Fo² - Fc²)²)/(No - Np)]¹/².
[b] R₁ [F² > 2σ(F²)] = Σ||Fo| - |Fc||/Σ|Fo|.
[c] wR₂ (all) = [Σ(w(Fo² - Fc²)²)/Σ(w(Fc²)²)]¹/².
[d] Final HKLF 4 output contains 93344 reflections, Rint = 0.0708 (TWINABS-2012/1)
References for Supporting Information

[S1] I. D. Brown, *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*, 2nd ed., IUCr Monographs on Crystallography 27, Oxford University Press, Oxford, UK, 2016.

[S2] I. D. Brown, *Chem. Rev.* 2009, 109, 6858–6919.

[S3] bvparm2016.cif, *Accumulated Table of Bond Valence Parameters*, (IUCr) Bond valence parameters, http://www.iucr.org/resources/data/datasets/bond-valence-parameters, I. D. Brown, Brockhouse Institute for Materials Research, McMaster University, Hamilton, ON, Canada.

[S4] I. D. Brown, D. Altermatt, *Acta Crystallogr.* 1985, B41, 244–247.

[S5] K. O. Christie, E. C. Curtis, R. D. Wilson, *J. Inorg. Nucl. Chem., Supplement*, 1976, 28, 159–165.

[S6] H. H. Claassen, G. L. Goodman, J. G. Malm, F. Schreiner, *J. Chem. Phys.* 1965, 42, 1229–1232.

[S7] M. Al-Mukhtar, J. H. Holloway, E. G. Hope, G. J. Schrobilgen, *J. Chem. Soc. Dalton Trans.* 1991, 2831–2834.

[S8] J. F. Lehmann, D. A. Dixon, G. J. Schrobilgen, *Inorg. Chem.* 2001, 40, 3002–3017.

[S9] J. C. Bertolini, *J. Emerg. Med.* 1992, 10, 163–168.

[S10] D. Peters, R. Miethchen, *J. Fluorine Chem.* 1996, 79, 161–165.

[S11] E. B. Segal, *Chem. Health Saf.* 2000, 7, 18–23.

[S12] W. J. Casteel, D. A. Dixon, H. P. A. Mercier, G. J. Schrobilgen, *Inorg. Chem.* 1996, 35, 4310–4322.

[S13] A. A. A. Emara, G. J. Schrobilgen, *Inorg. Chem.* 1992, 31, 1323–1332.

[S14] J. F. Lehmann, H. P. A. Mercier, G. J. Schrobilgen, *Coord. Chem. Rev.* 2002, 233–234, 1–39.

[S15] J. G. Malm, C. L. Chernick, *Inorg. Synth.* 2016, 25, 15815–15829.

[S16] R. J. Gillespie, G. J. Schrobilgen, *Inorg. Chem.* 1974, 13, 765–770.

[S17] J. H. Holloway, G. J. Schrobilgen, *J. Chem. Soc. Chem. Commun.* 1975, 623–624.

[S18] B. E. Pointner, R. J. Suontamo, G. J. Schrobilgen, *Inorg. Chem.* 2006, 45, 1517–1534.

[S19] J. Shamir, J. Binenboym, H. H. Classen, *J. Am. Chem. Soc.* 1968, 90, 6223–6224.

[S20] J. T. Goettel, M. R. Bortolus, D. G. Stuart, H. P. A. Mercier, G. J. Schrobilgen, *Chem. Eur. J.* 2019, 25, 15815–15829.

[S21] APEX2, v.2014.9-0, Bruker AXS Inc., Madison, WI (2005–2014).

[S22] SAINT+ – Integration Engine, v.8.38A, Bruker AXS Inc., Madison, WI (1997–2013).

[S23] SADABS-2014/4 – Bruker AXS Area Detector Scaling and Absorption Correction, Bruker AXS Inc., Madison, WI, 2014.

[S24] XPRESS – Reciprocal Space Exploration, v.2014/2, Bruker AXS Inc., Madison, WI, 2014.

[S25] G. M. Sheldrick, *Acta Crystallogr.* 2015, A71, 3–8.

[S26] G. M. Sheldrick, *Acta Crystallogr.* 2015, C71, 3–8.

[S27] O. V. Dolomanov, L. J. Bourhis, R. J. Giddea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* 2009, 42, 339–341.

[S28] CELL_NOW – Program for Unit Cell Determination, v.2008/4, G. M. Sheldrick, Georg-August-Universität Göttingen, Germany, 2008.

[S29] TWINABS – Bruker AXS Scaling for Twinned Crystals, v.2012/1, Madison, WI, 2014.

[S30] DIAMOND – Visual Structure Information System, v.3.1, K. Brandenburg, Crystal Impact GbR, Bonn, Germany (1997–2005).

[S31] EMSL Basis Set Exchange, v.1.2.2, https://bse.pnl.gov/bse/portal, Environmental Molecular Science Laboratory, Pacific Northwest National Laboratory, Richland, WA.

[S32] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.
A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Lyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Marakuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. Daniels, D. Farkas, J. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc: Wallingford, CT, 2009.

[S33] GaussView, version 3.0; Gaussian Inc.: Pittsburgh, PA, 2003.

[S34] NBO 6.0, E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013.

[S35] Multiwfn, version 3.3.8; T. Lu, F. Chen, J. Comput. Chem. 2012, 33, 580–592.

[S36] E. F. Pettersen, T. D. Goddard, C. C. Huang, G. S. Couch, D. M. Greenblatt, E. C. Meng, T. E. Ferrin, J. Comput. Chem. 2004, 25, 1605–1612.