Structural Principles of the Coordination Number Eight: WF_8^{2-}, ReF_8^{2-}, and XeF_8^{2-}

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Abstract: WF_6, ReF_n ($n = 6$ and 7), and XeF_6 combined with NOF to give $(NO^+)_2WF_8^{2-}$, $(NO^+)_2ReF_8^{2-}$, and $(NO^+)_2XeF_8^{2-}$, respectively. Also NO_2F reacted with ReF_6 to form $(NO_2^+)_2ReF_8^{2-}$. $Cs_2XeF_8 \cdot 4BrF_5$ crystallized from a solution of Cs_2XeF_8 in BrF_5. These five compounds were subjected to X-ray structure determinations. The structure of $[NO(NOF)_2]^+IF_8^-$ was used as a standard for comparison. All anions exhibit square-antiprismatic geometry, independent of their electronic configurations. Bond lengths in ReF_8^{2-} and XeF_8^{2-} are larger than in WF_8^{2-} and IF_8^-, owing to the presence of nonbonding electrons. Deviations from the ideal structure in XeF_8^{2-} are attributed to cation–anion interactions.

Keywords
coordination geometry · fluorides · square antiprisms · structure elucidation

Introduction

Compounds with coordination numbers (CN) exceeding six do not normally have a single typical geometry, since there are several geometries that are energetically close and can be interconverted by small angular changes, with the possible exception of CN 12 (icosohedron). Many authors have dealt with the geometrical problems associated with higher coordination numbers, especially for CN 8, and models of ligand repulsion have been developed for this case.[1]

Burdett, Hoffmann, and Fay discussed the molecular orbital model of the CN 8 in all possible geometries (the square antiprism, trigonal dodecahedron, bicapped trigonal prism, cube, hexagonal bipyramid, square prism, and bicapped trigonal prism),[2] but two principal structures remain for CN 8: from the electrostatic viewpoint the square antiprism and the trigonal dodecahedron are very similar in energy. The cube and all other possible geometries are higher in energy owing to fairly large ligand repulsion.[1]

There are many examples for both the square-antiprism and the trigonal-dodecahedron geometries. One of the better known cases is $W(CN)_8^{4-}$, which is dodecahedral in $K_4W(CN)_8 \cdot 2H_2O$ and square-antiprismatic in $H_4W(CN)_8 \cdot 6H_2O$.[3–5] In these and many other cases the structures are in part dominated by strong interionic forces, resulting in considerable deviations from the ideal geometries.

To establish the principal structure of CN 8, it would be preferable to determine the structures of uncharged AB_8 molecules, since cation–anion interactions, which may be stabilizing geometries that might not otherwise be energy minima, would then be eliminated. However, no such molecules are known, and reports on the isolation of the most likely candidates, XeF_8 and OsF_8, have been refuted.[6, 7] Our goal is therefore to study anions possessing the smallest possible charge. Previously, we have reported that IF_8^- is a highly regular square antiprism.[8] Its intraionic bond lengths and angles are used here as a standard reference. ReF_8^- should exist but so far all attempts to obtain single crystals have failed.[9] If we include doubly charged anions in our study, the number of available octafluoro anions increases, but greater care is then needed to take into account possible influences of intermolecular forces on the structures.

Since all the anions that were investigated in this study are square antiprismatic, we need only discuss this geometry. A square antiprism is a highly symmetric arrangement of ligands, which can be described fully by only two parameters, namely, the distance between central atom and ligand, and the angle describing the elongation or flatness of the square antiprism. Kepert suggested to use the angle α between the S_8 axis and the central atom ligand bond (Fig. 1).[1] This angle is the angle between two adjacent ligands within one hemisphere and the central atom, or by $\alpha = \gamma/2$, where γ is the angle between opposite ligands within one hemisphere. If the interligand distances between the two hemispheres is assumed to be equal to the interligand distance within each of the hemispheres (hard-sphere model), than this angle α is 59.26°. A soft-sphere model results in $\alpha = 57.1°$ if a repulsion energy law of $1/r^6$ is assumed.[1]

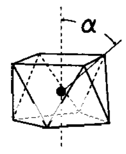

Fig. 1. Definition of α in a regular square pyramid.

The structures presented here will be checked against this ideal behavior. In particular, we will address the following questions: What are the possible differences in bond length? What is the torsional angle between the two squares (ideally 45°)? To what extent do the four ligands in one hemisphere deviate from

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planarity? Are the two planes parallel to one another? How close is the angle α to the ideal value? The structures will also be discussed in terms of cation–anion interactions. Furthermore, an answer to the question of the steric activity of nonbonding electrons (in ReF_8^{2-} and XeF_8^{2-}) will be suggested.

Results and Discussion

IF_8^-: The existence of $NO^+IF_8^-$, formed by the reaction of IF_7 with NOF, was first reported by Adams.[10] However, subsequent crystal structure determination proved this product to be $[NO(NOF)_2]^+IF_8^-$.[8a] Since the cation is quite large and short cation–anion contacts are absent, we will use the square-antiprismatic structure of IF_8^- as a standard for comparison. In the unit cell there are two crystallographically independent IF_8^- anions, which are virtually identical; the 16 different bond lengths are very much alike (187.9(5)–190.4(4) pm), as are the angles α (57.65 and 57.61°). The IF_8^- anion can also combine with the $(CH_3)_4N^+$ cation,[8a, b] but a fourfold disorder of the anion prevents a precise structural description in this case.[8a]

WF_8^{2-}: The ability of WF_6 to react with alkali metal fluorides has previously been established,[11, 12] but information on the structure of the resulting product is limited to the vibrational spectra, which are similar to those of Na_3TaF_8. The latter is square-pyramidal, according to its rather unreliable X-ray structure determination, and also exhibits very strong cation–anion interactions.[13] WF_6 and NOF have been combined to give $(NO^+)_2WF_8^{2-}$. The Raman spectrum was tentatively assigned in terms of a square antiprismatic symmetry.[14]

We synthesized $(NO)_2WF_8$ by reaction of WF_6 with NOF and obtained colorless single crystals. The crystal structure shows that the WF_8^{2-} ion is a very regular square antiprism (Fig. 2). Owing to the mirror plane in the space group *Pnma*, the eight fluorine atoms are represented by five independent positions. Bond lengths are as regular as in IF_8^-, and the slightly elongated bonds have the shortest contacts to the nitrogen atom of the NO^+ cation. Owing to symmetry constraints, the first set of four fluorine atoms lie in plane; the second set are also close to planar. The average angle α for all fluorine atoms relative to the S_8 axis is 57.50°, virtually identical to the value found in IF_8^-. The various criteria for ideal square-antiprismatic behavior and the actual values observed for this and all other anions are summarized in Table 1.

ReF_8^{2-}: Salts containing the ReF_8^{2-} ion have been reported earlier.[12, 14, 15] The violet color that we found for $(NO^+)_2ReF_8^{2-}$ and $(NO_2^+)_2ReF_8^{2-}$ raises some doubt as to whether the previously reported yellow compounds contained the ReF_8^{2-} anion. Preparing ReF_6 free of ReF_7 and $ReOF_5$ is not a trivial matter. Hence contamination by salts such as $A^+ReF_8^-$ (yellow?), $A^+ReOF_6^-$ (colorless),[15] $A^+ReF_7^-$ (orange),[16] and $A^+ReOF_5^-$ (green)[17] may be occurring. In reports by Nikolaev[17] pink salts of M_2ReF_8 (M = Na, K, Rb, Cs) are described, which react with excess ReF_6 to give yellow ReF_7^- compounds. A low-precision crystal structure determination for K_2ReF_8 gave results similar to those reported here.[18]

The violet color of the ReF_8^{2-} salts facilitates their visual detection, even when large amounts of by-products are formed. In HF or CH_3CN solution, the violet color is not observed, because the anion is present as ReF_7^-; ReF_8^{2-} is only formed upon crystallization. In this paper the crystal structures of $(NO^+)_2ReF_8^{2-}$ and $(NO_2^+)_2ReF_8^{2-}$ are reported. The latter was prepared by reaction of ReF_6 with NO_2F. The former was synthesized from ReF_7 and NOF. The reaction is slow, probably because ReF_7 is first reduced to ReF_6.

$(NO^+)_2ReF_8^{2-}$ is isotypic to $(NO^+)_2WF_8^{2-}$ (Fig. 2), but the Re–F bonds are on average 3 pm longer than the W–F bonds. This is attributed to the presence of a d^1 electron in ReF_8^{2-}, which expands the anion. The square antiprism of ReF_8^{2-} with α = 57.80° differs very little from IF_8^- and WF_8^{2-}; this indicates that the d^1 electron has virtually no specific geometrical effect.

$(NO_2^+)_2ReF_8^{2-}$ has eight crystallographically independent fluorine atoms. The ReF_8^{2-} anion is particularly regular with α = 57.87° (Table 1 and Fig. 3).

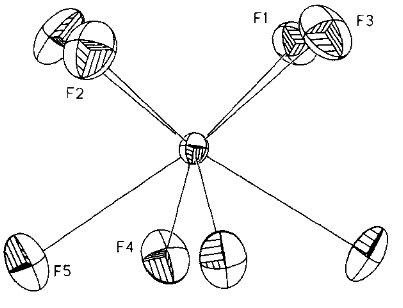

Fig. 2. Ortep plot of the anions WF_8^{2-} and ReF_8^{2-} in $(NO^+)_2WF_8^{2-}$ and $(NO^+)_2ReF_8^{2-}$, respectively (ellipsoids at the 50% probability level). The vibrational amplitudes of WF_8^{2-} are shown; those of ReF_8^{2-} are marginally smaller.

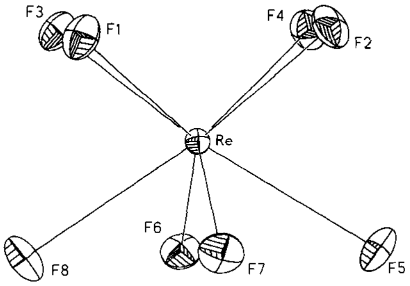

Fig. 3. Ortep plot of the ReF_8^{2-} anion in $(NO_2^+)_2ReF_8^{2-}$ (ellipsoids at the 50% probability level).

Table 1. Characteristics of square-antiprismatic geometries.

	ideal	$[NO(NOF)_2]^+IF_8^-$	$(NO^+)_2WF_8^{2-}$	$(NO^+)_2ReF_8^{2-}$	$(NO_2^+)_2ReF_8^{2-}$	$(NO^+)_2XeF_8^{2-}$	$(Cs^+)_2(BrF_4)_4XeF_8^{2-}$
bond lengths [pm]	equal	187.9–190.4(4)	190.4–193.5(2)	191.8–195.6(3)	191.0–195.3(3)	193.8–215.1(1)	195.4–207.5(4)
α_{av} [°] [a]	57.16 [b]	57.65 [c] 57.61	57.50	57.80	57.87	57.93	57.85
max. dev. from best planes [pm]	0 0	1(2) 1(2) 3(3) 4(4)	0 [d] 3.1(23)	0 [d] 2.3(17)	2.0(3) 0.8(3)	0 [d] 2.0(4)	0 [d] 3(1)
parallelity of best planes [°]	0	0.3(5) 1.0(5)	1.6(3)	1.2(2)	0.27(9)	1.71(8)	0.9(3)

[a] α: angle as defined in Figure 1. [b] Calculated for a soft-sphere model with a repulsion energy law $\approx 1/r^6$. [c] $NO^+(NOF)_2IF_8^-$ contains two crystallographically independent anions. [d] Enforced by crystal symmetry.

XeF_8^{2-}: As early as 1973 the crystal structure of $(NO^+)_2XeF_8^{2-}$ was determined.[19] The large vibrational amplitudes and estimated standard deviations reported in this work left room for discussion as to whether the nonbonding electron pair was sterically active. Indeed the basically square-pyramidal geometry appeared to be somewhat distorted. We have redetermined the crystal structure with the best precision available to us, and have also obtained a structure of a solvate $(Cs^+)_2XeF_8^{2-}\cdot 4BrF_5$.

$(NO^+)_2XeF_8^{2-}$ is crystallographically identical to $(NO^+)_2WF_8^{2-}$ and $(NO^+)_2ReF_8^{2-}$ (space group, special and general positions; see Fig. 4 and Table 2). This square antiprism is a little distorted. Bond lengths vary from 193.8(2) to 215.1(1) pm (cf. 194.6–209.9 reported previously[19]). The average angle $\alpha = 57.93°$, calculated from angles between 56.16 and 59.34°, may therefore not be meaningful. The two F4 atoms with very long bonds to Xe are those that have three short contacts to the nitrogen atoms of NO^+ (Table 3). The four F atoms in the one hemisphere with short bonds to Xe all have F···N contacts above 300 pm.

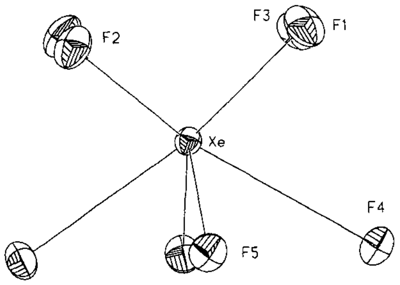

Fig. 4. Ortep plot of the XeF_8^{2-} anion in $(NO^+)_2XeF_8^{2-}$ (ellipsoids at the 50% probability level).

Table 3. Selected bond lengths [pm], contact distances [pm], and bond angles [°] with standard deviations in parentheses.

$(NO^+)_2WF_8^{2-}$					
W–F1	192.4(4)	F2···N2	280.0(8)	F1-W-F3	73.2(1)
W–F2	190.5(5)	F3···N2	242.0(7)	F2-W-F3	73.3(2)
W–F3	190.4(4)	F4···N1	246.6(7)	F4-W-F5	71.9(2)
W–F4	193.1(3)	F5···N1	258.7(8)	F4-W-F4	75.4(2)
W–F5	194.2(4)	F5···N2	249.8(7)	F5-We-F5	73.4(2)
$(NO^+)_2ReF_8^{2-}$					
Re–F1	193.2(4)	F2···N2	281.0(7)	F1-Re-F3	73.8(1)
Re–F2	191.0(4)	F3···N2	242.9(6)	F2-Re-F3	73.6(1)
Re–F3	191.8(3)	F4···N1	247.7(6)	F4-Re-F5	72.7(1)
Re–F4	193.5(3)	F5···N1	257.2(6)	F4-Re-F4	74.9(3)
Re–F5	195.1(3)	F5···N2	248.1(6)	F5-Re-F5	74.3(2)
$(NO_2^+)_2ReF_8^{2-}$					
Re–F1	191.8(2)	F1···N1	258.0(4)	F1-Re-F2	74.1(1)
Re–F2	190.5(2)	F3···N1	260.5(4)	F2-Re-F4	73.7(3)
Re–F3	194.6(2)	F3···N2	254.6(4)	F3-Re-F4	73.4(1)
Re–F4	194.0(2)	F4···N1	251.3(4)	F1-Re-F3	74.0(1)
Re–F5	194.3(2)	F4···N2	271.6(4)	F5-Re-F6	73.6(1)
Re–F6	191.8(2)	F5···N1	252.3(4)	F5-Re-F7	73.1(1)
Re–F7	192.7(2)	F5···N2	2.579(4)	F6-Re-F8	73.1(1)
Re–F8	193.2(2)	F7···N1	2.794(4)	F7-Re-F8	74.1(3)
		F8···N2	2.530(4)		
$(NO^+)_2XeF_8^{2-}$					
Xe–F1	200.3(1)	F4···N1	237.0(2)	F1-Xe-F3	73.32(4)
Xe–F2	193.8(1)	F4···N2	240.8(2)	F2-Xe-F3	73.70(4)
Xe–F3	194.41(9)	F4···N2	245.7(2)	F4-Xe-F5	72.80(3)
Xe–F4	215.19(9)	F5···N1	249.5(2)	F4-Xe-F4	74.00(5)
Xe–F5	203.9(1)			F5-Xe-F5	75.45(6)
$(Cs^+)_2XeF_8^{2-}\cdot 4BrF_5$					
Xe–F1	195.4(6)	Br1···F4	276.6(4)	F1-Xe-F3	74.2(2)
Xe–F2	197.2(5)	Br1···F5	274.0(4)	F2-Xe-F3	73.4(1)
Xe–F3	196.3(4)	Br2···F4	276.0(4)	F4-Xe-F5	74.3(2)
Xe–F4	206.2(4)	Br3···F5	281.0(4)	F4-Xe-F4	73.0(2)
Xe–F5	207.5(4)			F5-Xe-F5	71.9(2)

In the crystal structure of $(Cs^+)_2XeF_8^{2-}\cdot 4BrF_5$ the anion is less distorted. This material was obtained as colorless needles by crystallization of $(Cs^+)_2XeF_8^{2-}$ from BrF_5 at 60 °C with slow cooling. The incorporation of BrF_5 molecules into the structure has the fortunate effect that the XeF_8^{2-} anion is much less disturbed by cation–anion interactions. The structure (Fig. 5) is almost tetragonal with the crystallographic *pseudo*fourfold axis being identical to the S_8 axis of the square antiprism. Full tetragonal symmetry is not reached only because two BrF_5 units (Br2 and Br3) are rotated by approximately 45° (see Fig. 5). The five crystallographically different Xe–F bonds are in the 195.4(6)–207.5(4) pm range, and the two hemispheres of fluorine atoms are much more parallel to one another than in $(NO^+)_2XeF_8^{2-}$ (see Table 1). One hemisphere of fluorine atoms has four shorter bond lengths, and the other four longer ones. As can be seen in the side view (Fig. 5, bottom), the structure is a layered one. The four lower F atoms are in a plane with a BrF_5 layer and (Xe)–F···Br contacts of 274–281 pm (Table 3) lengthen the Xe–F bonds. The four upper F atoms with shorter bonds to Xe are in a plane with Cs cations, but Cs···F contacts all exceed 309.2 pm. The variation of Xe–F bond lengths is larger than in WF_8^{2-} and ReF_8^{2-}, but this seems to be typical for xenon. In the recently established crystal structure of pentagonal-prismatic $XeOF_5^-$ the chemically equivalent five basal fluorine atoms also

Table 2. Crystallographic data.

	$(NO^+)_2WF_8^{2-}$	$(NO^+)_2ReF_8^{2-}$	$(NO_2^+)_2ReF_8^{2-}$	$(NO^+)_2XeF_8^{2-}$	$(Cs^+)_2(BrF_4)_4XeF_8^{2-}$
M_r	395.87	398.22	430.22	343.30	1248.76
T [K]	125	125	125	120	120
space group	*Pnma*	*Pnma*	*Pbca*	*Pnma*	*Pnma*
a [pm]	888.6(2)	893.6(2)	977.7(2)	883.1(1)	1209.9(1)
b [pm]	575.0(1)	580.1(3)	1186.0(2)	589.7(1)	1240.4(1)
c [pm]	1246.1(2)	1238.0(4)	1236.7(2)	1286.9(2)	1554.9(2)
V [10^6 pm^3]	636.7(2)	641.1(8)	1434.0(4)	670.2(1)	2333.5(3)
Z	4	4	8	4	4
abs. coeff [mm^{-1}]	18.3	19.1	17.1	5.3	11.6
θ_{max} [°]	30	35	40	40	30
reflns collected	1061	1721	4164	2219	2342
reflns observed	982	1482	3910	2077	2339
refined parameters	70	70	136	71	172
R	0.025	0.029	0.027	0.019	0.032
$wR2$	0.064	0.070	0.067	0.055	0.069
goodness of fit	1.278	1.175	1.103	1.04	1.04

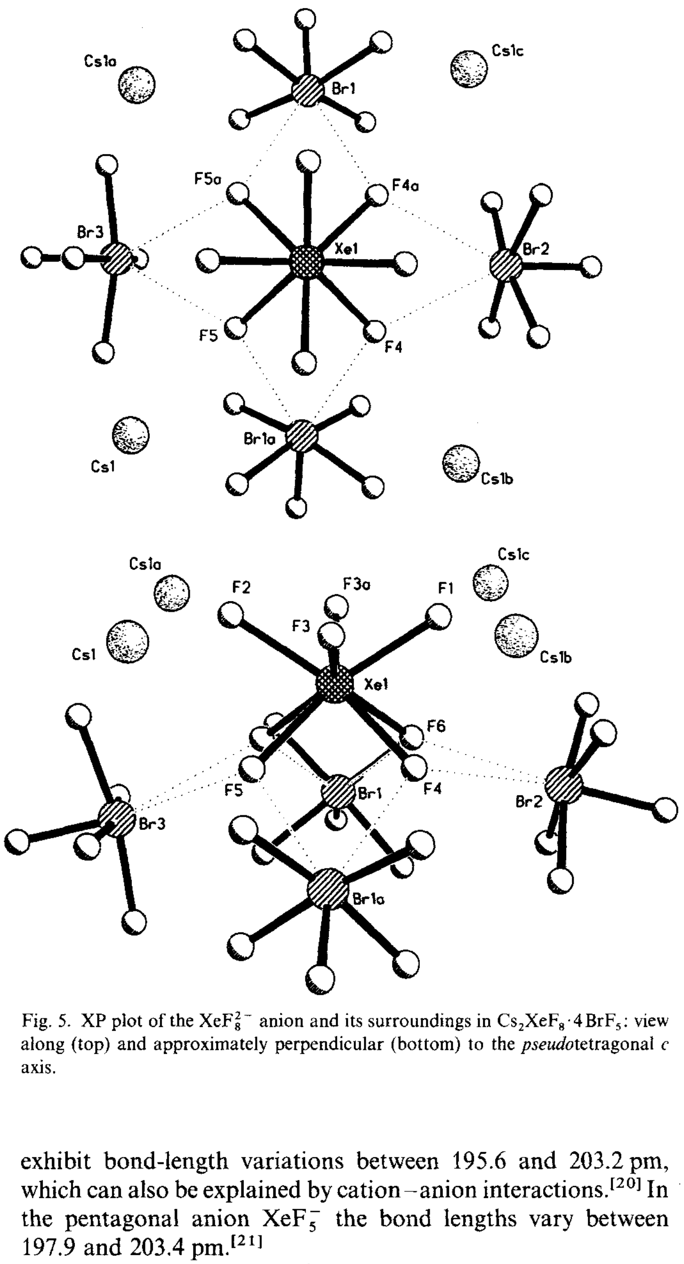

Fig. 5. XP plot of the XeF_8^{2-} anion and its surroundings in $Cs_2XeF_8 \cdot 4BrF_5$: view along (top) and approximately perpendicular (bottom) to the *pseudo*tetragonal *c* axis.

exhibit bond-length variations between 195.6 and 203.2 pm, which can also be explained by cation–anion interactions.[20] In the pentagonal anion XeF_5^- the bond lengths vary between 197.9 and 203.4 pm.[21]

The Xe–F bonds in XeF_8^{2-} are considerably longer than the I–F bonds in IF_8^-. This might be attributed to a shielding of the xenon atom by a centrosymmetric electron pair and an increased polarity of the central atom–fluorine bonds due to the double negative charge.

Conclusion

The structures presented here indicate that the square archimedean antiprism is the principal structure for coordination number eight, especially for eight equivalent ligands that are not involved in chelation, bridging bonds to neighboring atoms, or other stronger interionic interactions. Furthermore, these square antiprisms are all very close to ideal geometries, that is, they are neither elongated nor compressed along the S_8 axis. The d^1 electron in ReF_8^{2-} and the nonbonding electron pair in XeF_8^{2-} have no apparent steric influence, apart from causing a general bond lengthening. Obviously, the steric activity of the nonbonding pair diminishes drastically upon crowding, as can be seen from the sequence XeF_5^+ [22] (strong effect), XeF_6 (effect still structurally determining),[23] XeF_7^- (weak effect),[24] and XeF_8^{2-} (no effect). The same trend is observed when the number of ligands is held constant but the central atom size is reduced:[25] IF_6^- and XeF_6[23] (effect structurally determining) SeF_6^{2-}[26] (C_{3v} structure, weak effect), and BrF_6^-[26–27] (octahedral structure). Fluorine can be viewed as a ligand with σ-acceptor and π-donor properties, and the conclusions reached here for the CN 8 might be entirely different for ligands of different character. Not even the omnipresent octahedral structure for the CN 6 is retained in the case of $W(CH_3)_6$.[28]

Experimental Procedure

General: ^{19}F NMR spectra were measured on a FX90Q instrument (JEOL, Japan) at 84.25 MHz, $CFCl_3$ as external standard. Raman spectra: Cary instruments, model 82, argon ion laser excitation. IR spectra: Perkin Elmer 983. X-ray: Enraf Nonius CAD4 four-cycle spectrometer, $Mo_{K\alpha}$, graphite monochromator. Moisture-sensitive materials were handled in a dry-box with <0.1 ppm H_2O. Elemental analyses were performed by Beller, Göttingen (Germany).

Starting materials: WF_6 (98%) was obtained commercially and used as such. Commercial BrF_5 was purified before use by fluorination with elemental fluorine in a stainless steel pressure vessel to free it from BrF_3 and Br_2, and by subsequent vacuum distillation. Pure ReF_6 [29], ReF_7 [30], XeF_6 [31], NO_2F [32], and NOF [33] were obtained by literature methods. Cs_2XeF_8 was obtained by reaction of previously melted and ground CsF with excess XeF_6, as described in ref. [34].

$(NO^+)_2WF_8^{2-}$: WF_6 (0.91 g, 3.05 mmol) and NOF (0.29 g, 5.98 mol) were condensed on a glass vacuum line into a Teflon-FEP (perfluoroethene–propene copolymerizate) tube and sealed. Reaction started at −78 °C and was complete at −20°C. After the mixture had been maintained at this temperature for several days, all volatile components were pumped off, leaving a colorless powder. Recrystallization from dry CH_3CN at −40 °C afforded colorless single crystals. $N_2O_2WF_8$ (395.9); calcd N 7.08, O 8.08, W 46.44, F 38.4; found N 7.0 (08.6 diff.), W 46.0, F 38.4. Raman (cryst., cm^{-1}): $\tilde{\nu}$ = 2330.5 m, 2320.5 m, 1001.5 m, 983 m, 715.5 s, 661.5 vs, 615 s, 490 brs, 416 s, 352 s, 327 m.

$(NO^+)_2ReF_8^{2-}$: ReF_7 (1.2 g, 3.76 mmol) and NOF (0.45 g, 9.18 mmol) were condensed on a metal vacuum line into a Teflon-FEP tube and sealed. Immediately a powder consisting of yellow and violet microcrystals was formed. After the mixture had been maintained at −78 °C for 2 d, the tube was opened, and excess NOF was pumped off at −20 °C. The solid was recrystallized from anhydrous HF (bright green solution). HF diffused over several weeks through the plastic wall, and violet $(NO^+)_2ReF_8^{2-}$ and green $(NO^+)ReOF_5^-$ crystals were formed. Raman (cryst., cm^{-1}): $\tilde{\nu}$ = 2332.5 m, 2325 m, 1021 s, 646.5 vs, 504 vs, 423 n, 357 vs, 317 vs.

$(NO_2^+)_2ReF_8^{2-}$: ReF_6 (1.5 g, 15 mmol) and NO_2F (1 g, 15.38 mmol) were condensed on a metal vacuum line into a Teflon-FEP tube. The tube was sealed and maintained at −78 °C overnight. The volatiles were then pumped off at −20 °C. The remaining powder was dissolved in a little anhydrous HF. The solution was an intense green. After diffusion of HF through the plastic wall, large violet $(NO_2^+)_2ReF_8^{2-}$ and green $NO_2^+ReOF_5^-$ crystals remained. $N_2O_4ReF_8$ (430.2); calcd. N 6.56, F 35.33; found N 6.40, F 37.5. Raman (cryst., cm^{-1}): $\tilde{\nu}$ = 1406 s, 646.5 vs, 517 s, 420.5 m, 143.5 s, 125 s.

$(NO^+)_2XeF_8^{2-}$ (cf. ref. [19]): XeF_6 (0.9 g, 3.7 mmol) and NOF (0.3 g, 6 mmol) were condensed on a metal vacuum line into a Teflon-FEP tube. The tube was sealed and kept at 25 °C. A small temperature gradient was applied, and slow sublimation within days afforded colorless single crystals.

$(Cs^+)_2XeF_8^{2-} \cdot 4BrF_5$: XeF_6 (1.7 g, 6.9 mmol) was condensed on a metal vacuum line into a Teflon-FEP tube, containing CsF (0.4 g, 2.6 mmol). The mixture was stored at room temperature for 3 d. The excess XeF_6 was pumped off at 0 °C, pure BrF_5 added (3 mL), and the tube sealed. Colorless needles were obtained by slowly cooling from 40 to 4 °C.

Crystal structure determinations (see also Table 2): Tubes containing single crystals were opened into the mouth of a special apparatus for handling moisture, oxygen, and temperature sensitive compounds [35]. A suitable crystal was selected and mounted on a glass tip with perfluoropolyether and adjusted on the Enraf Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation, graphite monochromator. Cell dimensions were established by fine orientation of 25 reflections with $20 < \theta < 25°$. Data were collected in the ω-scan mode with a maximum of 60 s for each reflection, depending on intensity, and leaving 25% of measuring time for background measurements. After Lorentz polarization correction the structures were solved with the program

SHELXS86 [36] and refined with SHELXL93 [37]. Absorption corrections were performed by the Difabs method [38].

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59138.

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