

F₂Al(μ - η^2 : η^2 -O₂)AlF₂: An Unusual, Stable Aluminum Peroxo Compound

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The oxidation processes in the industrial production of aluminum from cryolite melts are not fully understood. Oxidation of AlOF_2^- leads initially to AlOF_2 radicals. The structure of the AlOF_2 dimer and several oxidized and reduced forms of this compound are investigated by theoretical methods and compared to analogous boron and gallium compounds. The thermodynamic stability of these compounds is investigated. It is shown that the dimeric compound of AlOF_2 contains a symmetric peroxo bridge and is unexpectedly stable toward decomposition.

Introduction

Aluminum is produced in large amounts by the Hall–Héroult industrial process through electrolysis of Al_2O_3 dissolved in cryolite (Na_3AlF_6) melts.¹ In this process aluminum is formed at the cathode, and depending on whether carbon or inert electrodes are used, carbon dioxide and oxygen are formed at the anode. Depending on the composition of the electrolyte mixture, different oxyfluoroaluminates are present,² with AlOF_2^- , $\text{Al}_2\text{OF}_6^{2-}$, and $\text{Al}_2\text{O}_2\text{F}_4^{2-}$ considered to be the most important species.³ Depending on their relative concentrations and the applied anode potential when using carbon anodes, investigations of the oxidation product have shown that it can vary from CO and CO_2 to metastable COF_2 and CF_4 .⁴ No detailed studies have been conducted of the oxidation process at inert anodes, but various publications and analyst reports⁵ indicate the reaction efficiencies are less, thus raising the question about alternative oxidation products.

In mass spectrometric studies of the vapor species AlF_3 , Al, and Al_2O_3 at temperatures between 1453 and 1675 K, a low-intensity peak was assigned to AlOF_2^+ ions.⁶ It was assumed that these supposed AlOF_2^+ ions originate from AlOF_2 radicals, and the heat of formation of AlOF_2 was estimated to be -265.2 ± 3.0 kcal/mol.³ Vibrational frequencies⁷ and their partition functions⁸ were calculated

from these data by comparing AlOF_2 with BOF_2 and estimating its bonding parameters. The thermodynamic data were used to calculate the composition of AlO_xF_y surface films deposited by dc reactive sputtering.⁹

Still, AlOF_2 remained elusive up to now, with only tentative proof of its existence. The question arises of whether such an unusual compound with aluminum in the formal oxidation state +4 can be isolated and studied in matrix isolation or if it is even sufficiently stable to be synthesized. If the reported data are accurate, then AlOF_2 could be metastable species in cryolite melts. This could then contribute to the efficiency lowering that has been experienced during the aluminum production.

Peroxo complexes of main group elements are very rare.¹⁰ The first aluminum peroxide species XAlO_2 (X = F, Cl, Br) was detected by matrix isolation IR spectroscopy by Schnöckel and co-workers in the reaction of subvalent halides AlX (X = F, Cl, Br) with O_2 .^{10,11} Bridging μ - η^2 : η^2 -O₂ complexes are known for transition metals and lanthanides, actinides and copper peroxides have been found in important biological systems as oxidation catalysts,¹² e.g., in hemocyanin,¹³ and a number of μ - η^2 : η^2 -O₂ Cu(I) complexes have been synthesized recently.¹⁴ μ - η^2 : η^2 -O₂ peroxo complexes have also been characterized for several lanthanides and actinides,¹⁵ but only

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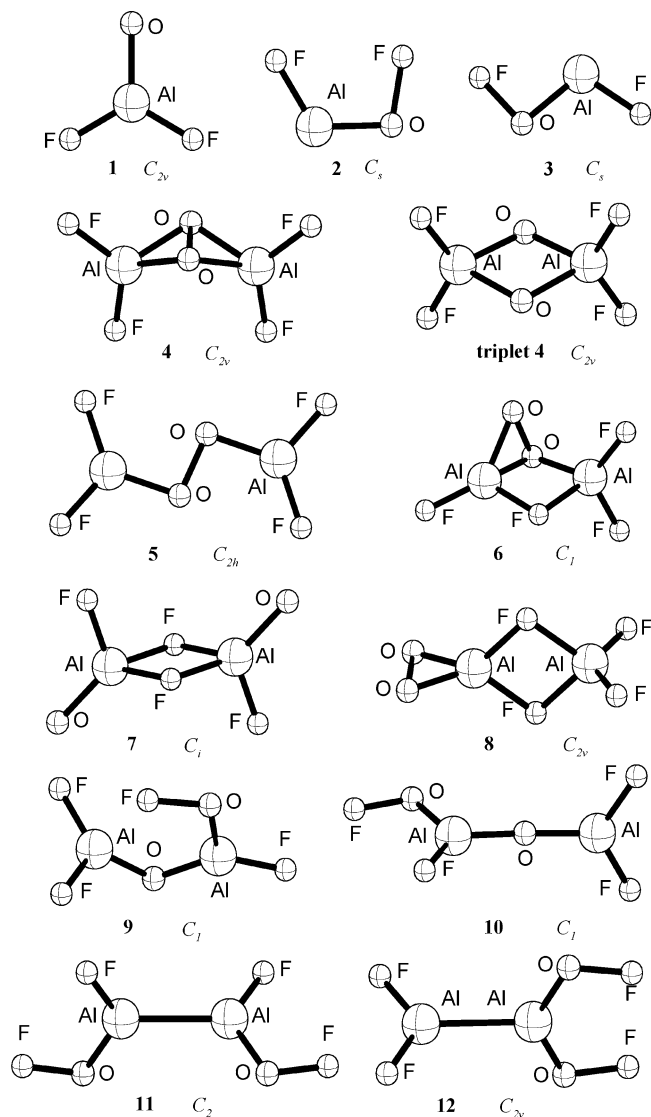


Figure 1. Different optimized isomers of $AlOF_2$ and $[AlOF_2]_2$. The point group symmetry is also given. All structures are minima, except structure 5, which is a first-order saddle point on the potential energy surface (see the text).

a few complexes with bent $\mu-\eta^2:\eta^2-O_2$ coordination to the metal centers are known.¹⁶

Computational Details

To study the stability of $AlOF_2$, we carried out ab initio calculations for a number of AlO_xF_y species (Figure 1) and for comparison for the isoelectronic boron and gallium species. All structures were fully optimized within the stated symmetry constraints (Figure 1) with GAUSSIAN98.¹⁷ First, preoptimizations at the B3LYP level with LANL2DZ pseudopotentials and basis sets were performed followed by all-electron MP2 calculations using augmented cc-pVDZ basis sets.¹⁷ All optimized structures are available in Cartesian coordinates as Supporting Information (Table S1). For gallium we used Ahlrich's TZV basis set.¹⁸ Vibrational

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Table 1. Geometrical Parameters of MOX_2^n ($n = 0, -1$) Compounds at the MP2 Level of Theory (Distances, Å; Angles, deg)

	M–O	M–F	F–M–F	F–M–O
BOF_2	1.376	1.341	121.0	119.5
BOF_2^-	1.287	1.432	105.6	127.2
$AlOF_2$	1.766	1.667	121.8	119.1
$AlOF_2^-$	1.681	1.730	102.7	128.7
$GaOF_2$	1.802	1.739	119.7	120.2
$GaOF_2^-$	1.715	1.809	99.9	130.1

Table 2. Energies (kcal/mol; Including Zero-Point Vibrational Energy Correction) for $AlOF_2$ and $[AlOF_2]_2$ Species Relative to the Most Stable Isomer **1** for the Monomers and **4** for the Dimers

structure	MP2	CCSD(T)	structure	MP2	CCSD(T)
2	103.6	102.6	8	32.7	31.9
3	104.4	104.0	9	53.3	49.9
4 ($S = 1$) ^b	37.8	23.3	10	57.4	57.4
5	32.4	33.0	11	234.6	222.5
6	6.0	5.2	12	235.3	223.5
7	(–95.8) ^a	20.4			

^a Single-reference MP2 can sometimes give unreliable results for compounds in high oxidation states, where a single-reference coupled cluster procedure such as CCSD(T) still performs well (the T_1 diagnostic gave a value of 0.0126 for compound 7). ^b Triplet state (see the text).

frequencies were computed for all optimized structures to verify that a minimum was obtained. Subsequent coupled cluster (CCSD(T)) single-point energy calculations were performed with MOLPRO2002¹⁹ at the optimized MP2 geometries to obtain more accurate energy differences, especially for the high oxidation state compounds considered. The relative MP2 energies were in good agreement with the CCSD(T) energies for most of the compounds studied here, and with a few exceptions, the B3LYP structures closely resemble those of MP2.

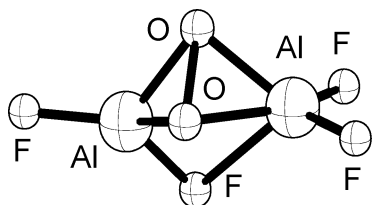
Results and Discussion

Three minima were found for monomeric radical $AlOF_2$, Figure 1. The bond distances and angles for the global minimum structure are given in Table 1. The hypofluorites **2** and **3** are considerably higher in energy than the conventional structure **1** (Table 2), which as expected represents a 2B_2 state of C_{2v} symmetry with the radical centered almost exclusively on the oxygen atom. Since $AlOF_2$ is a radical, its dimer $[AlOF_2]_2$ was also studied (Tables 2 and 3). Eight low-energy isomers representing minima on the potential energy surface were found. The global minimum structure **4** can be de-

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Table 3. Geometrical Parameters of $(\text{MOF}_2)_2^{n-}$ Compounds (M = B, Al, and Ga; $n = 0-2$) at the MP2 Level of Theory (Distances, Å; Angles, deg) (F1 and F2 Bound to the Same Metal Atom (M1) and F3 and F4 to M2, with F3 Being *cis* to F1)

	M-O	M-F1/3	M-F2/4	O-O	F-M-F	M-O-O	M-O-M	O-M-O	O-M-F1/3	O-M-F2/4	F1-M-O-M	F2-M-O-M	O-M-O-M
$(\text{BOF}_2)_2$	1.386	1.339	1.332	1.462	120.9	107.8	142.8	37.2	114.7	120.9	0.0	0.0	0.0
$(\text{BOF}_2)_2^-$	1.507	1.404	1.403	1.994	110.4	48.6	91.1	82.8	116.1	114.6	89.7	139.8	26.0
$(\text{BOF}_2)_2^{2-}$	1.474	1.480	1.480	2.206	102.8	41.6	83.1	96.9	114.5	114.5	120.9	120.9	0.0
$(\text{AlOF}_2)_2$	1.872	1.665	1.667	1.638	121.3	64.1	112.5	51.9	116.7	115.6	60.9	146.7	43.3
$(\text{AlOF}_2)_2^-$	1.816	1.709	1.708	2.244	108.6	51.9	102.2	76.3	117.6	117.0	126.7	101.2	13.2
$(\text{AlOF}_2)_2^{2-}$	1.813	1.762	1.762	2.617	100.5	43.8	87.6	92.4	116.3	116.3	121.0	121.0	0.0
$(\text{GaOF}_2)_2$	1.938	1.737	1.735	1.661	122.4	64.6	111.2	50.7	116.7	114.9	57.6	148.9	46.2
$(\text{GaOF}_2)_2^-$	1.866	1.783	1.783	2.316	107.5	51.6	103.3	76.7	117.6	117.6	114.5	114.5	0.0
$(\text{GaOF}_2)_2^{2-}$	1.871	1.840	1.840	2.693	99.0	44.0	88.0	92.0	116.8	116.8	121.6	121.6	0.0

**Figure 2.** Transition state between structures **4** and **6** (see Figure 1).

scribed as two AlF_2 units that are bridged by a side-on-connected peroxide ion: $\text{F}_2\text{Al}(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)\text{AlF}_2$. An end-on-connected peroxide ion ($\mu\text{-}1,2\text{-O}_2$) in **5** represents a transition state with an imaginary frequency of only 11 cm^{-1} , which is rather low for a barrier of 32.4 kcal/mol (Table 2). The dihypofluorites **11** and **12** are very high in energy compared to all other isomers and will not be discussed here. Similarly, the hypofluorites **9** and **10** are still over 50 kcal/mol above the global minimum structure **4** (Table 2). The somewhat lower energy of these isomers compared to the dihypofluorites is explained by the favored Al-O-Al bond. Structures **6** and **8** also contain peroxide ions, with **6** being surprisingly stable and only 5.2 kcal/mol higher in energy than **4**, even though one of the oxygen atoms is bound to only one Al atom. **6** is the product of the rotation of one AlOF_2 group with respect to the other. The transition state (Figure 2) of this rotation is 10.5 kcal/mol (MP2, 10.3 kcal/mol) above the minimum structure **4**. $[\text{AlOF}_2]_2$ is the reduced species of $[\text{AlOF}_2]_2^{2-}$, and one has to consider a triplet state as a possible candidate for the electronic ground state of $[\text{AlOF}_2]_2$. However, this state lies well above the singlet state (Table 2).

A comparison with the analogous boron and gallium compounds is interesting. The overall structures shown in Figure 1 can serve for a comparison here. For $[\text{BOF}_2]_2$ structure **5** is now a minimum on the potential energy surface resembling the end-on-connected peroxide ion with a trans bent B-O-O-B unit, thus giving boron the formal oxidation state $+3$ as is usually expected. Hence, in the boron compound there are only two boron-oxygen bonds in contrast to four metal-oxygen interactions in the aluminum and gallium species, the latter preferring the same geometrical arrangement as the corresponding aluminum compound **4**.

The question arises of whether there is a bond between the two bridging oxygen atoms in the $\text{F}_2\text{M}(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)\text{MF}_2$ compounds of Al and Ga or not. In the latter case one would assign the formal oxidation state $+4$ to the metal center. The O-O distances in the Al and Ga compounds are 1.638 and 1.661 Å , respectively, and significantly longer compared to

that of molecular oxygen (1.208 Å), but shorter than in the corresponding anions $[\text{MOF}_2]_2^-$ (Al, 2.244 Å ; Ga, 2.316 Å) and $[\text{MOF}_2]_2^{2-}$ (Al, 2.617 Å ; Ga, 2.693 Å), indicating a bonding interaction between the two oxygen atoms. For FAIO_2 , Schnöckel and co-workers find a similar O-O bond length of 1.65 Å .^{10,11} Other O-O bonds of $\mu\text{-}\eta^2\text{:}\eta^2$ peroxides are however shorter and closer to the O-O bond length of sodium peroxide with 1.49 Å .^{1,20} Lanthanide peroxides have bond lengths between 1.55 Å ²¹ and 1.65 Å ,¹⁵ the dicopper peroxide mentioned above has a O-O bond length of 1.43 Å ,¹² and a bent peroxy complex of vanadium has a O-O bond length of 1.467 Å .¹⁶ The O-M-O bond angle (Al, 51.9° ; Ga, 50.7°) is smaller than in FAIO_2 (58.4°), but larger than in similar lanthanide (41°), copper (43°), or vanadium (43°) complexes. The M-O₂-M unit in the copper and lanthanide complexes is planar; the V-O-V angle in the vanadium complex is 99° compared to 112.5° (Al) and 111.2° (Ga). B3LYP calculations also give a planar $\text{Al}(\text{O}_2)\text{-Al}$ unit in contrast to MP2 (here the D_{2h} structure is a first-order transition state with 2.2 kcal/mol above the minimum arrangement), which shows that the O₂ out of plane motion follows a path along a shallow potential energy surface. Finally, a bond critical analysis using Bader's atoms-in-molecules (AIM) method clearly reveals a bond path between the two oxygen atoms (Figure 3) with a sizable density. Furthermore, a natural bond orbital (NBO) analysis²² clearly shows a bonding orbital between the two oxygen atoms of almost exclusively oxygen p-character with a small (4.5%) s-admixture. The bonding orbital between the two oxygen atoms is also shown in Figure 3. The Mulliken charges (Table 4) show that during successive oxidation of $[\text{MOF}_2]_2^{2-}$ the charge at the oxygen atoms diminishes, giving the oxygen atoms in $\text{F}_2\text{M}(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)\text{MF}_2$ the formal oxidation state $+1$, as expected for a peroxide ion.

In the gas phase the monoanion $[\text{AlOF}_2]_2^-$ is slightly less stable (1.8 kcal/mol) than the dianion $[\text{AlOF}_2]_2^{2-}$ (reaction V in Figure 4 and Table 5), which implies that the doubly negatively charged species is stable with respect to electron loss. This is different for the boron compound. Here the dianion is 16.3 kcal/mol higher in energy than the monoanion and therefore not stable with respect to electron loss. As expected, the energy required for the reduction of the

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Table 4. Mulliken Charges of Different $(MOF_2)_2^{n-}$ Compounds (M = B, Al, and Ga; $n = 0-2$) at the MP2 Level

	$[BOF_2]_2^{2-}$	$[BOF_2]_2^-$	$[BOF_2]_2$	$[AlOF_2]_2^{2-}$	$[AlOF_2]_2^-$	$[AlOF_2]_2$	$[GaOF_2]_2^{2-}$	$[GaOF_2]_2^-$	$[GaOF_2]_2$
M	1.60	1.59	1.53	2.36	2.06	2.34	2.22	2.24	2.24
O	-1.03	-0.70	-0.51	-1.65	-1.01	-0.77	-1.53	-1.13	-0.78
F	-0.79	-0.71	-0.44/-0.58	-0.85	-0.77	-0.78	-0.85	-0.81	-0.72

Table 5. Reaction Energies for the Oxidation of $[MOF_2]_x^{n-}$ Species (M = B, Al, and Ga; Including Zero-Point Vibrational Energy Correction; All Values in kcal/mol) (See Figure 4 for Details)

reaction	(a) $[BOF_2]_x^{n-}$		(b) $[AlOF_2]_x^{n-}$		(c) $[GaOF_2]_x^{n-}$	
	MP2	CCSD(T)	MP2	CCSD(T)	MP2	CCSD(T)
I	92.8	85.7	84.9	76.4	91.3	81.7
II	50.2	48.6	-39.1	-43.5	-19.6	-24.2
III	-50.7	-41.9	-90.5	-82.0	-73.0	-63.7
IV	84.7	80.9	118.3	114.3	129.1	123.8
V	-11.4	-16.3	9.7	1.8	17.6	8.3
VI	96.1	97.2	108.7	112.5	111.6	115.5

Table 6. Energies for the Decomposition of $[MOF_2]_2$ Compounds (kcal/mol; Zero-Point Vibrational Energy Corrections Included)

	MP2	CCSD(T)
$[BOF_2]_2 \rightarrow B_2OF_4 + 0.5O_2$	-32.0	-29.7
$[AlOF_2]_2 \rightarrow Al_2OF_4 + 0.5O_2$	-6.9	-3.9
$[AlOF_2]_2 \rightarrow Al_2F_4 + O_2$	105.7	102.4
$[AlOF_2]_2 \rightarrow Al_2O_2F_2 + F_2$	133.6	131.8
$[AlOF_2]_2 \rightarrow AlOF + AlF_3 + 0.5O_2$	83.0	88.9
$[GaOF_2]_2 \rightarrow Ga_2OF_4 + 0.5O_2$	-17.2	-14.2

monoanion to the neutral dimer (VI) increases slightly from boron (97.2 kcal/mol) to aluminum (112.5 kcal/mol) and gallium (115.5 kcal/mol); hence, the overall oxidation energy from the dianion to the neutral dimer (IV) increases from boron (80.9 kcal/mol) to aluminum (114.3 kcal/mol) and gallium (112.5 kcal/mol), Table 5.

The dimerization of the monomer radical MOF_2 to $[MOF_2]_2$ is exothermic for all three elements (Figure 4 and Table 5), but the dimerization of the aluminum compound is far more exothermic (-82.0 kcal/mol) than the dimerization of both the gallium (-63.7 kcal/mol) and the boron (-41.9 kcal/mol) compounds. Hence, the aluminum compound $[AlOF_2]_2$ shows an unusually high stability. The lower dimerization energy of BOF_2 explains that the vibrational spectrum of the BOF_2 radical has already been observed^{23,24} and was recently assigned.²⁵ The difference in the dimerization energy between aluminum and gallium is explained by the stronger aluminum-oxygen bond. The dimerization of the monomer anion (reaction II) is endothermic for boron (48.6 kcal/mol), but exothermic for both aluminum (-43.5 kcal/mol) and gallium (-24.2 kcal/mol).

To address the stability of $[AlOF_2]_2$, we investigated several pathways for its decomposition under loss of oxygen or fluorine to form known AlO_xF_y species (Table 6). The formation of Al_2OF_4 and half a dioxygen molecule is slightly exothermic (-3.9 kcal/mol) and further supported by entropy effects, but the formation of Al_2F_4 and one dioxygen molecule (102.4 kcal/mol; remember the shallow potential energy surface for the O_2 out of plane motion), the formation of $Al_2O_2F_2$ and one difluorine molecule (131.8 kcal/mol),

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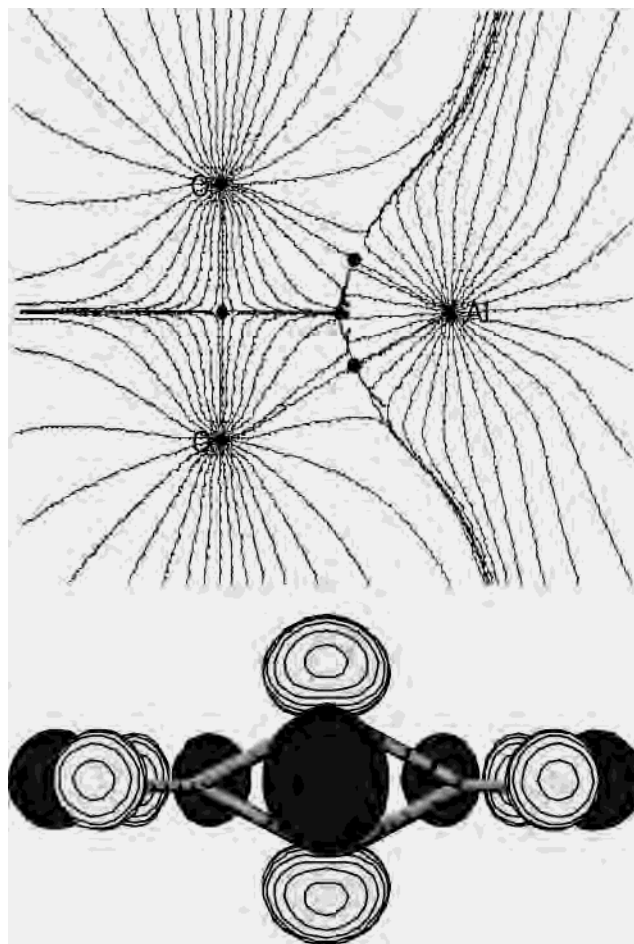


Figure 3. Gradient vector field of **4** with bond paths and bond/ring critical points obtained from an AIM analysis. The density at the critical point between the two oxygen atoms is 0.17 au, and the Laplacian of the electron density is $-\nabla^2\rho(\mathbf{r}_c) = 0.35$ au. The binding orbital consisting mainly of $O(2p)$ is shown below. The same plane definition was used in both pictures.

and the formation of $AlOF$, AlF_3 , and half a dioxygen molecule (88.9 kcal/mol) are all strongly endothermic. Taking into account the activation barrier for an oxygen loss through collision with another molecule (which is difficult to estimate), a relatively high stability for $[AlOF_2]_2$ is expected. The formation of B_2OF_4 under loss of half a dioxygen molecule from $[BOF_2]_2$ is -29.7 kcal/mol more exothermic than for the aluminum compound due to the different structure of the boron compound. The decomposition of $[GaOF_2]_2$ to form Ga_2OF_4 and $0.5O_2$ (-14.2 kcal/mol) is also more exothermic than for $[AlOF_2]_2$, but less so compared to that of $[BOF_2]_2$.

Conclusions

During the electrolysis of Al_2O_3 -cryolite mixtures, voltages of 4.0-4.7 V are applied at temperatures between 940 and 980 °C.¹ The reduction of $[AlOF_2]_2^{2-}$, which is one of the components of the melt,^{2,3} to $[AlOF_2]_2$ requires 5.0 eV

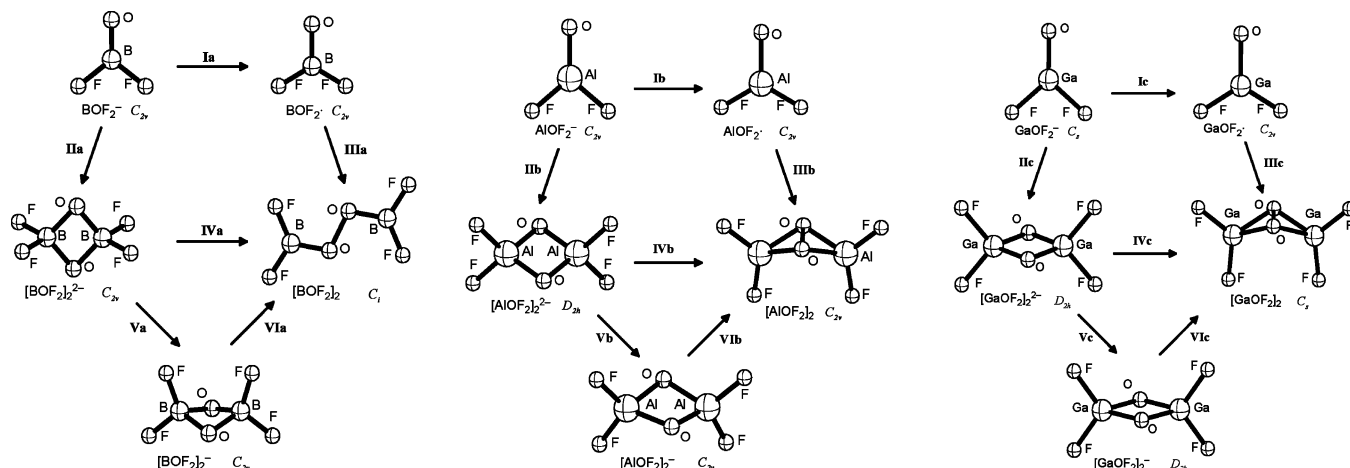


Figure 4. Reactions between $[\text{MOF}_2]_x^-$ species ($M = \text{B}, \text{Al}, \text{and Ga}$). All structures shown are optimized MP2 geometries.

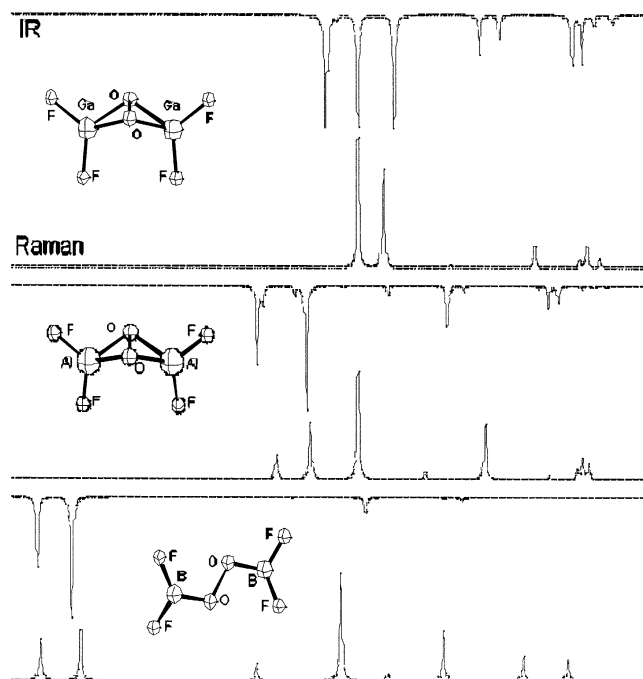


Figure 5. Simulated vibrational spectra for $[\text{MOF}_2]_2$ compounds ($M = \text{B}, \text{Al}, \text{and Ga}$; frequencies (cm^{-1}) and relative intensities from MP2 calculations; the Raman spectrum was calculated with the Hay/Wadt basis set for cost reasons). The most intense lines belong to motions of the oxygen atoms.

in the gas phase. Even if the conditions of the salt melt, which should lower the energy of the dianion and thus increase the energy gap, are considered, it is possible that $[\text{AlOF}_2]_2$ is formed during the electrolysis with inert electrodes in the

melt, which should be further investigated and may have a high impact on this important economical process. Using the same procedure for estimating the heat of formation as from the mass spectrometric data,⁶ the calculated value of AlOF_2 is 239.9 kcal/mol and that of $[\text{AlOF}_2]_2$ 562.7 kcal/mol.

Our calculations suggest that $[\text{AlOF}_2]_2$ is a stable molecule with a novel structure for main group metal peroxides. Its production and characterization by matrix isolation spectroscopy or, more optimistically, isolation in solid form should be possible. It may also be present in the electrolysis of cryolite melts with inert electrodes and explain the decreased efficiency in this process. For straightforward identification we include in Figure 5 the simulated infrared and Raman spectra for all $[\text{MOF}_2]_2$ ($M = \text{B}, \text{Al}, \text{and Ga}$) compounds studied.

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Note Added after ASAP: The formula in the first sentence of the Results and Discussion section was incorrect in the version of this article posted ASAP on January 17, 2004. The corrected version appeared on January 22, 2004.

Supporting Information Available: All optimized structures at the MP2 level of theory as Cartesian coordinates (Table S1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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