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ScienceDirect
Journal of Fluorine Chemistry 129 (2008) 82–90
JOURNAL OF FLUORINE CHEMISTRY
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Greedy Ag(II) oxidizer: Can any inorganic ligand except fluoride endure its presence in ionic solids?[☆]

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Received 18 June 2007; received in revised form 29 August 2007; accepted 1 September 2007
Available online 6 September 2007

Abstract

The available thermodynamic data for a variety of oxides, chlorides and fluorides of various elements and for the AgF_2/AgF, AgF_2/Ag_2O redox pairs are analyzed in detail. We show that AgF_2 is capable of oxidizing a vast majority of oxides and chlorides with the concomitant evolution of O_2 or Cl_2, respectively. Interesting cases are discussed of the inertness of sulfates, perchlorates and nitrates against AgF_2. In addition, perfluorinated amines should not be susceptible to oxidation and they might form complexes with Ag^{II}. The DFT calculations support the view that Ag^{II} transfers substantial share of d^9 hole into the oxide and chloride bands in hypothetical model compounds.

Keywords: Chlorides; Fluorides; Oxides; Redox reactions; Silver

1. Introduction

With its impressive value of the *second* ionization potential (ca. 21.46 eV), which is slightly larger than the respective value for the 'noble' Xe (21.22 eV), silver ranks *second to none among all metallic elements* except for the group 1 metals (Fig. 1). In other words, divalent silver (Ag^{II}) is the most potent one-electron oxidizer among all chemically attainable metal M^{2+} cations [1]. This unusual feature of Ag^{II} is reflected in the value of a standard redox potential, E^0, for the Ag^{II}/Ag^{I} redox pair, being as positive as +1.98 V in an acidic aqueous environment [2].

The nature of divalent silver imposes strict restrictions on the chemical composition of ligands, which can bind to it without immediately being oxidized. The Ag^{II} cation is found in nearly 100 compounds, all of which contain simple fluoride (F^-) or complex fluoride ligands (for example, BF_4^-, SbF_6^-, etc. [1]). Divalent silver is in principle incompatible with oxides and chlorides; AgO is better formulated as $Ag^{I}[Ag^{III}O_2]$, while genuine $AgCl_2$ has never been achieved [3]. In the gas phase, the ground state of '$AgCl_2$' could be described as Ag^{I} bound to two chloride anions with one hole in their π/p orbitals [4]. Nevertheless, indications can be found in the literature that Ag^{II} might exceptionally exist in the spatial vicinity of covalently bonded O^{2-} (as in the adduct of AgF_2 with WOF_4 [5], or in the complexes with fluorosulfate anion, SO_3F^- [6] and triflate anion, $CF_3SO_3^-$ [7]). It can even bind to a lone pair of a covalently bound N (as in several complexes of Ag^{II} with a cyclic tetraza ligand [8], pyridine [9] or bipyridyl [10]).

Extension of the number of ligands which could bind to Ag^{II} would be extremely valuable in the context of a possible generation of a 2D structure which contains the flat [AgF_2] sheets. Compounds with such structural unit have been previously proposed to exhibit high-temperature superconductivity [1,11], similarly to the known related layered oxides of Cu^{II} (see Ref. [1]). Therefore, the thermochemistry of Ag^{II}, in particular of AgF_2 (the only commercially available salt of Ag^{II}), should be carefully re-examined. With this in mind, in the present work the thermodynamics of over 200 redox reactions of AgF_2 are analysed, and several anionic and neutral species

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[☆] This contribution commemorates the 45th anniversary of Neil Bartlett's preparation of the first noble gas compound with the use of a potent PtF_6 oxidizer.

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doi:10.1016/j.jfluchem.2007.09.001

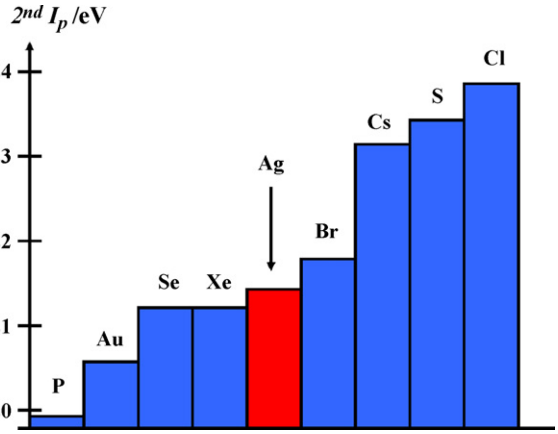


Fig. 1. The values of the second ionization potential for several elements including Ag.

which could withstand the presence of Ag^{II} without being oxidized, are identified.

2. Results

2.1. Thermodynamic parameters and the thermal decomposition of AgF_2

AgF_2 is a brown [12] light-sensitive paramagnetic salt (which orders ferromagnetically below 163 K), with a density of 4.58 g cm^{-3} [2]. It has a moderate thermal decomposition temperature of 690 °C [2], which is significantly larger than the respective values for several thermally unstable higher fluorides of transition metals, such as CuF_3 (−40 °C, in KHF_2-rich HF), AgF_3 (20 °C, in HF), PrF_4 (90 °C), and MnF_4 (150–320 °C). Thermal stability of AgF_2 is in fact comparable to that of TlF_3 (550 °C), TbF_4 (550 °C), and CeF_4 (600 °C), – all of which are strong oxidizers – which also makes AgF_2 the least thermally stable *difluoride* of a metallic element. Its decomposition occurs according to the equation:

$$AgF_2 \rightarrow AgF + (1/2)F_2, \qquad (1)$$

where a slightly nonstoichiometric, yellowish AgF is produced; stoichiometric AgF is colourless.

The structure of AgF_2 is orthorhombic [1,13] in a distorted variant of the fluorite (CaF_2) structure. The Jahn–Teller (JT) effect, typical of the d^9 species (Fig. 2), gives rise to a severe 4 + 2 distortion of the $[AgF_6]$ octahedron, with four short and two long Ag–F contacts. The $[AgF_{4/2}]$ unit is polymerized in two dimensions and the $[AgF_2]$ sheets are substantially puckered. Indeed, AgF_2 may be classified as a 'polymeric' or 'substantially covalent' fluoride, similarly to BeF_2; AgF_2 is sparingly soluble in anhydrous HF (48 mg in 100 g of HF at 11.5 °C), similarly to MgF_2 and ZnF_2, while many other related difluorides (MF_2, where M = Ca…Ba, Cd, Hg) exhibit excellent solubility in this solvent. All alkaline earth difluorides are substantially ionic and can easily be melted and evaporated into a gas phase without decomposition, in strong contrast to AgF_2.

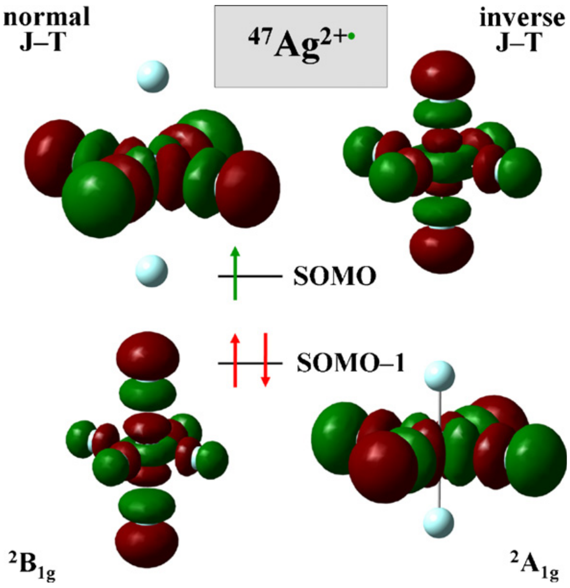


Fig. 2. The Jahn–Teller effect for Ag^{2+} (d^9 system). Ag^{2+} cation shows a remarkable flexibility of its first coordination sphere and can exhibit either a normal or an inverse JT effect. The arrangement of the two uppermost d orbitals in the elongated O_h (4 + 2) ligand field (normal JT effect, left), and in the compressed O_h (2 + 4) ligand field (inverse JT effect, right) [14].

The *Lange's Handbook of Chemistry* (15 ed.) [15] is the source of thermodynamic data for AgF_2. The value of $\Delta H_\mathrm{f}^\circ$ is −360 kJ mol^{-1} [16]. The lattice energy of AgF_2 equals 2942 kJ mol^{-1} [17], in excellent agreement with the theoretical value of 2919 kJ mol^{-1} [17]. The lattice energy of AgF_2 is nearly identical to that of MgF_2 (2957 kJ mol^{-1} from thermochemical cycle, 2913 kJ mol^{-1} calculated [17]), while the radius of the Mg^{2+} cation is ~0.2 Å smaller than that of Ag^{2+}. This feature testifies to the substantial covalent contribution to the Ag–F chemical bonding, which makes the Ag–F bonds reasonably stiff.

The entropy factor of AgF_2 apparently has never been estimated before. Fortunately, it turns out that the entropies of formation of the difluorides of Mg^{2+}, Ca^{2+}, Zn^{2+} and Cd^{2+} [15] are very similar to one another (Table 1). The ionic radii of the respective cations are either slightly smaller (Mg, Zn), or slightly larger (Ca, Cd) than that of Ag^{2+}. We may therefore assume that the $(-T\,S_\mathrm{f}^\circ)$ term for AgF_2 will be similar to those of its congeners. To account for the small variations of S_f° with the size of cation (which is related to the softest phonon modes via vibrational entropy factor) we have simply adopted here an arithmetic average of those (52.4 kJ mol^{-1}) as an estimate of the $(-T\ S_\mathrm{f}^\circ)$ term for AgF_2. Combining the enthalpy and entropy terms, one obtains $\Delta G_\mathrm{f}^\circ$ of about −307.6 kJ mol^{-1}.

The $(-T\,S_\mathrm{f}^\circ)$ factor for AgF_2 yields the *absolute* entropy of AgF_2 of 69.8 J mol^{-1} K^{-1}. This value is very close to 71.3 J mol^{-1} K^{-1}, which may be obtained from the molar volume of AgF_2 using the Jenkins and Glasser approach [18].

The thermodynamic parameters of AgF_2 and the respective values for AgF and F_2 [15] can now be used to estimate the thermochemistry of the reaction (1). It turns out that the

Table 1
The standard entropy of formation ($-T\,S^\circ_\mathrm{f}$) factor (at 298 K) for the difluorides of Zn, Ca, Cd and Mg, and an estimate of the entropy factor for AgF_2 as an arithmetic average of these

Compound	$-T\,S^\circ$ (kJ mol^{-1})
ZnF_2	51.1
CaF_2	52.6
CdF_2	52.7
MgF_2	53.1
AgF_2	(52.4)

reaction (1) is endothermic, with $\Delta H^\circ_\mathrm{r}$ of +155.4 kJ mol^{-1}, and ($-T\,\Delta S^\circ_\mathrm{r}$) of -64.65 kJ mol^{-1}. Thus, AgF_2 is a thermodynamically stable compound at room temperature.

It is possible to estimate the 'thermodynamic' thermal decomposition temperature of AgF_2, using the condition: $\Delta G^\circ_\mathrm{r} = 0$ at $T = T_\mathrm{dec}$; a value of 716 K is obtained. This is much smaller than the experimental value of the thermal decomposition temperature (963 K), but the calculation does not account for: (i) kinetic barriers; (ii) dependence of the thermodynamic parameters on temperature; (iii) differences in the specific heat of the substrates and products of reaction (1), which may be large, since F_2 is a gas; (iv) the fact that the AgF product is molten at the decomposition temperature of AgF_2. For example, correction by the value of the melting enthalpy of AgF + 16.7 kJ mol^{-1}, leads to a better value of the thermodynamic thermal decomposition temperature of AgF_2 (793 K). Last but not the least, the thermal decomposition of AgF_2 occurs slowly even below the onset value of 963 K. Therefore, the disagreement between the experimental and 'thermodynamic' values is understandable. A similar estimate of the 'thermodynamic thermal decomposition temperature' of $CuCl_2$ yields the value, which is *larger* by 176 °C than the experimental value of 300 °C.

We can now use the thermodynamic parameters of AgF_2 to estimate the thermochemistry of a set of redox reactions with AgF_2 as a substrate. It is expected that oxides and chlorides would be the least susceptible to oxidation among all non-fluoride anions, and therefore attention is concentrated mainly on these two types of binary salts and on their ternary derivatives. With very few exceptions only the salts of elements in their highest attainable oxidation states are considered (AgF_2 should oxidize most of low-valent species).

The standard enthalpies, $\Delta H^\circ_\mathrm{r}$, of close to 200 redox reactions are listed in the Supplementary material to this paper. For the most interesting cases, and whenever the entropy data were available for all substrates and products, we have also calculated the value of the free enthalpy of reaction, $\Delta G^\circ_\mathrm{r}$.

2.2. Redox reactions involving AgF_2

2.2.1. Binary oxides

We begin with simple binary oxides. Several types of reactions, Eqs. (2a)–(2c), as exemplified by Li_2O, are considered:

$$(1/2)\mathrm{Li_2O} + \mathrm{AgF_2} \rightarrow \mathrm{LiF} + \mathrm{AgF} + (1/4)\mathrm{O_2} \tag{2a}$$

$$\mathrm{Li_2O} + \mathrm{AgF_2} \rightarrow 2\mathrm{LiF} + (1/2)\mathrm{Ag_2O} + (1/4)\mathrm{O_2} \tag{2b}$$

$$\mathrm{Li_2O} + \mathrm{AgF_2} \rightarrow (1/2)\mathrm{Li_2O_2} + \mathrm{LiF} + \mathrm{AgF} \tag{2c}$$

These reactions differ in the outcome. Reaction (2a) leads to the evolution of all oxygen in the form of O_2; in reaction (2b) some oxygen is preserved in the system as Ag_2O; finally, the entire oxygen content is turned into a stable peroxide species in reaction (2c). For some binary oxide reagents, the corresponding peroxides are not known (for example, $B_2^{III}(O_2^{2-})_3$, and only reactions analogous to (2a) and (2b) have been considered.

All group 1 M_2O (M = Li...Cs, and H), group 2 MO (M = Be...Ba), group 12 (Zn...Hg), group 3 and group 13 M_2O_3 (Sc...La, B...Tl) oxides are significantly susceptible to oxidation by AgF_2. This feature should be related to the substantial basicity of the oxide anion (O^{2-}) linked to these cations via an ionic bonding. It is further confirmed by an increasing susceptibility of an oxide towards oxidation in descending the group of the Periodic Table (for example: from Be to Ba), and by large (relative) inertness of B_2O_3 and HgO, with the largest covalent contribution to element–O bonding within the analyzed set of compounds. Both B_2O_3 and HgO readily form stable ternary salts with more basic oxides, as exemplified by $NaBO_2$ and K_2HgO_2. DFT calculations show that the energy of reaction 41a in Supplementary material ((1/2)HgO + AgF_2) is equal to -2.9 kJ mol^{-1}, which is very close to the enthalpy of this reaction estimated from the thermodynamic data available (-1.7 kJ mol^{-1}).

The MO_2 oxides of the group 4 (M = Ti...Hf) and group 14 elements (M = C...Pb), and dioxides of Ce and Th further follow these trends. The majority of them could, in principle, be exothermically oxidized by AgF_2. There are two cases when the reaction is close to thermoneutral (GeO_2) or modestly endothermic (CO_2). In the case of CO_2, the entropy terms for the gaseous products (O_2, CF_4, COF_2) are still likely to overcome the small enthalpy term for the reactions listed.

Only three M_2O_5 oxides of the group 5 (M = V...Ta) and group 15 elements (M = N...As) seem to be stable against AgF_2 in reactions leading to corresponding pentafluorides; these are N_2O_5, V_2O_5 and As_2O_5 (no data are available for Sb and Bi derivatives). N_2O_5 is particularly stable (the NF_5 product is not, five F atoms cannot be easily crowded around a very small N^{5+}), even with respect to NOF_3 and NO_2F [19]. Although thermodynamic data are missing for $AsOF_3$, it is anticipated that the enthalpies of analogous reactions involving As_2O_5 might be slightly negative. Additional validation comes from the known large affinity of P, As, Sb and Bi towards F. In conclusion, N_2O_5 is the only pentaoxide, which indisputably should be unreactive towards AgF_2.

The cases of MO_3 trioxides of group 6 (Cr...W), group 16 (S...Te) and U, and the M_2O_7 heptaoxides of group 7 (Mn...Re) and group 17 (Cl...I), and of Np, are equally interesting as the case of the M_2O_5 species. Unfortunately, many fundamental thermodynamic data are missing. From the available data we can conclude that SO_3 undergoes slightly endothermic reactions leading to SF_6:

$$(1/6)SO_3 + AgF_2 \rightarrow (1/6)SF_6 + AgF + (3/2)O_2 \qquad (3a)$$

$$(1/3)SO_3 + AgF_2 \rightarrow (1/3)SF_6 + (1/2)Ag_2O + (1/4)O_2 \qquad (3b)$$

but slightly exothermic ones leading to SO_2F_2:

$$(1/2)SO_3 + AgF_2 \rightarrow (1/2)SO_2F_2 + AgF + (1/4)O_2 \qquad (3c)$$

$$SO_3 + AgF_2 \rightarrow SO_2F_2 + (1/2)Ag_2O + (1/4)O_2 \qquad (3d)$$

Reactions are endothermic between MoO_3 and AgF_2 yielding MoF_6 (the data for MoO_2F_2 are missing). Trioxides of larger, more polarizable hexavalent cores: Se, W and U, yield slightly negative values of the reaction enthalpies, and so should TeO_3.

The only heptaoxide, for which thermodynamic data are available, is thermodynamically unstable Cl_2O_7. It reacts endothermically with AgF_2 leading to ClO_3F. Possibly the explosive Mn_2O_7 should behave in a similar way. Heptaoxides of the heavier elements of group 7 and 17 and of neptunium, should be less stable.

No thermodynamic data are available for the MO_4 tetroxides (M = Ru, Os, Xe, Pu) or for the potential products of their reactions with AgF_2 (for example, MO_2F_4 species), and therefore these species are omitted in our analysis.

In order to better appreciate the important trends, a comparison is necessary of various oxides. In Fig. 3(a) and (b) are presented the values of the standard enthalpy, ΔH_r°, of the generalized reactions:

$$(2/n)E^{n+}O_{n/2} + AgF_2 \rightarrow (2/n)E^{n+}F_n + (1/2)Ag_2O + (1/4)O_2 \qquad (4a)$$

and

$$(1/n)E^{n+}O_{n/2} + AgF_2 \rightarrow (1/n)E^{n+}F_n + (1/2)AgF + (1/4)O_2 \qquad (4b)$$

for all oxides considered in this study.

The inertness of an $EO_{n/2}$ oxide towards AgF_2 usually increases with the increase of a maximum valence of the element E. This is well exemplified by the Rb…Mo series. This rule has very few exceptions; for example the inertness towards AgF_2 does not change monotonically in the (Ge, As, Se) set; in addition, Ag_2O is relatively more inert than CdO, while HgO than PbO_2.

Another important trend is related to the usual decrease of inertness in descending a group of the Periodic Table, for example for the (Be…Ba) series. However, this trend has more exceptions, notably an inverse order of inertness is observed for Rb and Cs, Al and Ga, Cd and Hg, Zr and Hf, and Ge and Pb. A substantial part of these deviations may be explained by an enhanced thermodynamic stability of a heavier oxide due to pronounced relativistic effects.

Both trends discussed above may be generalized in a single statement: if the oxide anion (O^{2-}) is bound to a very strong Lewis acid (C^{4+}, N^{5+}, S^{6+}, etc.) then it is much less susceptible to oxidation than if it is linked to a weak Lewis acid (Na^+, Ba^{2+}). Such behaviour may be easily rationalized in terms of the electron density available for withdrawal at the oxide anion. Bivalent nature of the oxide anion is another factor which promotes stability of oxides of the high-oxidation state elements; it is relatively easy to crowd four O atoms around, say, Mn^{7+} in Mn_2O_7, than seven F atoms in MnF_7. Indeed, MnF_7 has never been synthesized.

The inertness of selected binary oxides of chemical elements at their highest oxidation state, towards oxidation by AgF_2 (expressed by enthalpy effects only and taking into account also other reactions than (4a) and (4b)), is summarized in Fig. 4.

2.2.2. Peroxides

Peroxides of the general formula $E_n^{n+}(O_2^{2-})$ are considered to be 'an oxidized form of oxides', with the formal −1 oxidation state of O. At the first sight it might seem that peroxides should resist the AgF_2 oxidizer better than the corresponding oxides. It is however not true. The standard

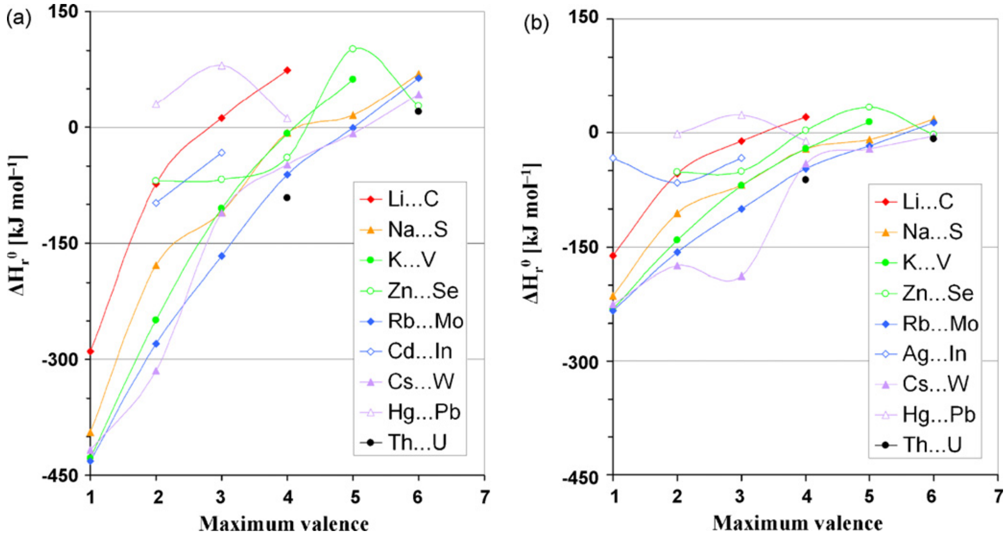
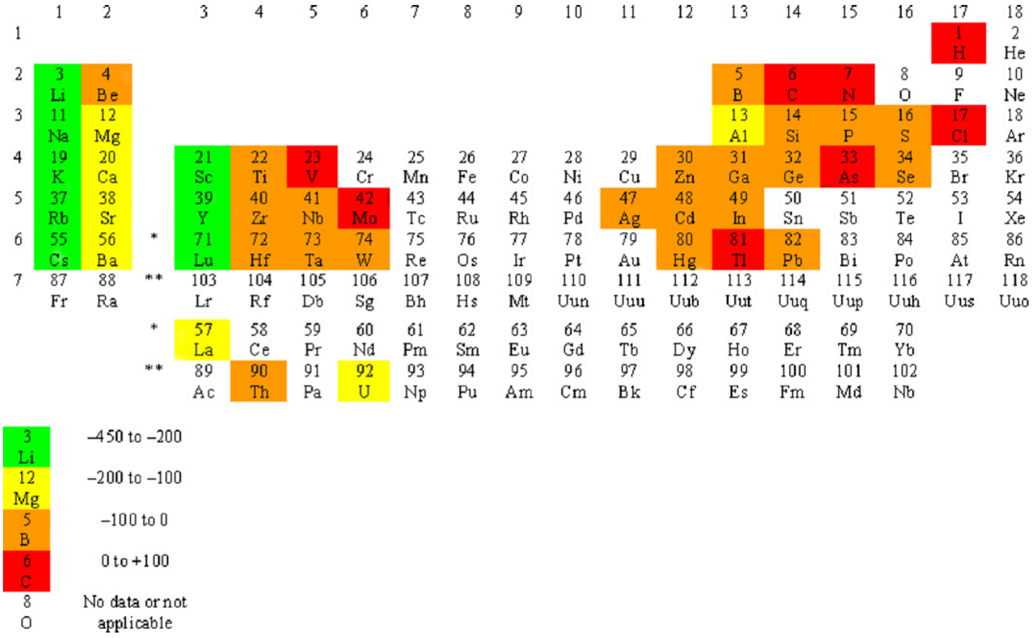


Fig. 3. Illustration of the standard enthalpy of (a) reaction (4a) and (b) reaction (4b); see text.



	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1																		🟥 1 H	2 He
2	🟩 3 Li	🟧 4 Be												🟧 5 B	🟥 6 C	🟥 7 N	8 O	9 F	10 Ne
3	🟩 11 Na	🟨 12 Mg												🟨 13 Al	🟧 14 Si	🟧 15 P	🟧 16 S	🟥 17 Cl	18 Ar
4	🟩 19 K	🟨 20 Ca		🟩 21 Sc	🟧 22 Ti	🟥 23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	🟧 30 Zn	🟧 31 Ga	🟧 32 Ge	🟥 33 As	🟧 34 Se	35 Br	36 Kr
5	🟩 37 Rb	🟨 38 Sr		🟩 39 Y	🟧 40 Zr	🟧 41 Nb	🟥 42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	🟧 47 Ag	🟧 48 Cd	🟧 49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	🟩 55 Cs	🟨 56 Ba	*	🟩 71 Lu	🟧 72 Hf	🟧 73 Ta	🟧 74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	🟧 80 Hg	🟥 81 Tl	🟧 82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
			*	🟨 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			**	89 Ac	🟧 90 Th	91 Pa	🟨 92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 Nb		

🟩 3 Li	−450 to −200
🟨 12 Mg	−200 to −100
🟧 5 B	−100 to 0
🟥 6 C	0 to +100
8 O	No data or not applicable

Fig. 4. Illustration of the inertness of the selected binary oxides of the chemical elements at their highest oxidation state, towards oxidation by AgF_2, as judged from the more negative among enthalpies of reactions (4a) and (4b). The 'inertness islands' are marked in red. See text for details.

redox potential, E^0, of the $((1/2)H_2O_2/H^+, (1/2)O_2)$ pair (+0.70 V) is over 1 V *less* positive than the corresponding value for the $(H_2O/H^+, (1/2)H_2O_2)$ pair (+1.76 V). All stable peroxides (of Li…Cs and Ba) show significant propensity towards oxidation by AgF_2 (see Supplementary material). H_2O_2 behaves in a similar way, although its reaction with AgF_2 is much less exothermic than for the alkali- or alkali earth peroxides.

2.2.3. *Other oxogenic ligands*

In Section 2.1 was noted the substantial stability of selected *binary oxides* of high-oxidation state elements towards oxidation by AgF_2. Most of these oxides (such as CO_2, N_2O_5, V_2O_5) have acidic character and they form salts easily with the alkali or alkali earth metal oxides. It is therefore interesting to verify the propensity of the *ternary salts* of these oxides towards oxidation by AgF_2. The concept here is that if the acid–base reaction, such as for example:

$$K_2O + SO_3 \rightarrow K_2SO_4 \qquad (5)$$

has a substantial thermodynamic driving force, then, despite susceptibility of a base (here: K_2O) towards oxidation, the ternary salt may still retain inertness, typical of the acidic oxide (here: SO_3).

This hypothesis was tested for the following salts: metaborates ($B^{III}O_2^{-1}$), metaaluminates ($Al^{III}O_2^{-1}$), carbonates ($C^{IV}O_3^{-2}$), titanates ($Ti^{IV}O_3$), nitrates ($N^VO_3^{1-}$), metavanadates ($V^VO_3^{1-}$), sulfates ($S^{VI}O_4^{2-}$), chromates ($Cr^{VI}O_4^{2-}$), molybdates ($Mo^{VI}O_4^{2-}$), uranates ($U^{VI}O_4^{2-}$), perchlorates ($Cl^{VII}O_4^{1-}$) and periodates ($I^{VII}O_4^{1-}$) (data for metaphosphates, $P^VO_3^{1-}$, are not available). Analysis (Supplementary material) shows that only nitrates, sulfates, perchlorates and periodates would resist oxidation by AgF_2. All of these are rather weakly coordinating oxogenic anions, which can be used themselves (with the exception of inert sulfates) as oxidizers.

The inertness of these salts raises an interesting question. Could pseudobinary salts of Ag^{II}, such as sulfate or nitrate, be synthesized? And could more complex $K[AgF_2L]$ and $K_2[AgF_2L_2]$ compounds exist such as adducts of KNO_3 (or, respectively, K_2SO_4, $KClO_4$, KIO_4, KSO_3F and related KSO_3CF_3) with AgF_2, in an analogous manner as KF forms ternary $KAgF_3$ and K_2AgF_4 connections? Another important question is related to the possible existence of the mixed valence Ag^I/Ag^{II} salts, such as for example $Ag_2SO_4{\cdot}AgF_2$. The Ag^I/Ag^{II} mixed valent species are immensely rare, the fluorosulphate $Ag_2{}^IAg^{II}(SO_3F)_4$ being the only one of this kind (see Ref. [6]). Analysis of thermodynamics of various reactions involving salts of these anions suggests that, in analogy to perchlorato- and nitrato-complexes of Xe^{II}, at least part of the abovementioned compounds (including the mixed valent species), should be achievable, thus leading to significant extension of the chemistry of Ag^{II} beyond fluorine-based anions.

2.2.4. *Oxofluorides*

The case of WO_2F_2 [5] indicates that selected oxofluorides of elements at high-oxidation states might be stable against AgF_2, at least kinetically. This family of compounds contains several interesting members, such as M^VOF_3 (M = N…Sb, V…Ta, Pa), $M^{VI}O_2F_2$ (M = S…Te, Cr…W, U) and $M^{VII}O_3F$ (M = Cl…I, Mn…Re, Np). Unfortunately, the available thermodynamic data are very limited. Our analysis (Supplementary material) confirms that dioxodifluorides of S, W and U should be stable against AgF_2. It is therefore likely that analogous compounds of Se, Te, Cr and Mo might behave in a similar way, particularly those, which, similarly to WO_2F_2, are not gaseous at ambient conditions, but readily form extended solids of substantial lattice energy.

2.2.5. Water and simple acids

It is instructive to study the propensity of H_2O and 100% H_2SO_4 (pure liquids) to undergo oxidation by AgF_2. The reaction:

$$H_2O + AgF_2 \rightarrow 2HF_{(g)} + (1/2)Ag_2O + (1/4)O_2 \quad (6)$$

has a very slightly negative ΔG_r° of about -11.7 kJ mol^{-1}, at the *positive* ΔH_r° of +56.7 kJ mol^{-1}. Thus, the reaction between water and AgF_2 is endothermic, and occurs only due to the beneficial entropy factor (we do not take into account the formation of stable $HF \times (H_2O)_n$ solvates, which may turn the reaction exothermic). Freshly prepared AgF_2 immediately turns black in moist air. It seems that remarkable speed of this reaction must be due to some $Ag^{\bullet 2+}$-initiated free radical mechanism.

Pure H_2SO_4 is a powerful and oxidizing acid, which dissolves oxidatively upon heating selected electropositive metals (including Cu, Ag, Hg etc.). The reaction of SO_3 with water, which leads to H_2SO_4, is very exothermic. It is therefore interesting to learn that the reaction:

$$H_2SO_4 + AgF_2 \rightarrow (1/2)SO_3 + 2HF + (1/2)Ag_2SO_4 + (1/4)O_2 \quad (7)$$

is favoured thermodynamically ($\Delta G_r^\circ = -48$ kJ mol^{-1}), and despite the fact that ΔH_r° is in fact positive (+71.6 kJ mol^{-1}).

In conclusion, AgF_2 is capable of oxidizing water and should attack even very strong oxogenic acids, such as H_2SO_4. Reactivity of AgF_2 towards 100% H_2SO_4, and related HSO_3F and HSO_3CF_3, merits experimental verification.

2.2.6. Binary chlorides and oxochlorides

In contrast to oxides, nearly all higher chlorides studied could easily be oxidized by AgF_2. The thermodynamic data available for many monochlorides of alkali metals, and dichlorides of the alkali earth metals indicate that, without exception, they are susceptible to oxidation by AgF_2. This is also the case of $BeCl_2$ and $AlCl_3$, which form 1D polymeric chlorides, and of Ga_2Cl_6, with its appreciably covalent element–Cl bonds. In addition, DFT calculations show that the energy of reaction 72 in Supplementary material ($BeCl_2 + AgF_2$) is equal to -98.4 kJ mol^{-1}, which is close to the enthalpy of this reaction estimated from the thermodynamic data available (-109.9 kJ mol^{-1}).

The tetra-, penta- and hexachlorides of the high-oxidation state elements, such as M^{IV} (M = C...Ge, Ti...Hf, Th), M^{V} (M = P, Nb, Ta), and M^{VI} (M = Mo, U), behave in a similar manner. DFT calculations show that the energy of reaction ((1/4)$SiCl_4 + AgF_2$) (reaction 81 in Supplementary material) is equal to -90.7 kJ mol^{-1}, close to the enthalpy estimated from the thermodynamic data available (-76.6 kJ mol^{-1}). We anticipate that the remaining systems in this set for which the data is missing, *i.e.* M^{IV} (M = Sn), M^{V} (M = As...Bi, V, Pa), and M^{VI} (M = W, S...Te), should also show propensity towards oxidation. In conclusion we note that chlorides are in principle much more unstable in the presence of AgF_2 than the corresponding oxides.

The analysis of thermodynamic data reveals only five remarkable cases of inertness of a chloride towards AgF_2: (i) HCl, for which the redox process:

$$HCl + AgF_2 \rightarrow HF + AgF + (1/2)Cl_2 \quad (8)$$

is quite endothermic (+25.6 kJ mol^{-1}), and should occur only due to the favourable entropy term; (ii) $PbCl_4$, with the enthalpy of reaction close to null, hence it would certainly be overcome by entropy factor of gaseous Cl_2; (iii) explosive NCl_3, for which ΔG_r° should be close to null, due to canceling of the reaction enthalpy and entropy terms, and (iv) AgCl and (v) $AuCl_3$, with their positive reaction enthalpies (+77.8 and +73.4 kJ mol^{-1}, respectively) and positive ΔG_r° values.

The last two cases, (iv) and (v), are the most interesting. Recollect, Ag^{I} and Au^{III} form very firmly bound chloride complexes, notably $AgCl_2^-$ and $AuCl_4^-$. The presumed inertness of the two noble metal chlorides could thus be traced back to the large strength of the metal–Cl bonding, which is achieved via good overlap of Cl's 3p and transition metal valence d–s orbitals. Unfortunately, thermodynamic data is not available for $MAuCl_4$ and $MAgCl_2$, where M = Li...Cs, and therefore we cannot estimate at present if these complex salts would also endure oxidizing power of AgF_2. In addition, the DFT calculations show that the energy of reaction 71 in Supplementary material ($AgCl + AgF_2$) is equal to +6.8 kJ mol^{-1}, which is positive but very far from the enthalpy of this reaction estimated from the thermodynamic data available (77.8 kJ mol^{-1}). Therefore, it is advisable to verify this in experiment.

The tabularized data for simple oxochlorides is limited to three compounds only: SO_2Cl_2, WO_2Cl_2, and $WOCl_4$ (Table S6 in the Supplementary material). SO_2Cl_2 might react exothermically with AgF_2 while yielding SO_2F_2. Analogous reaction for WO_2Cl_2 cannot be evaluated due to lack of data for the WO_2F_2 product (importantly, our DFT calculations for the analogous reaction involving CrO_2Cl_2 yield the negative energy of redox reaction of -26.0 kJ mol^{-1} AgF_2). Interestingly, all other reactions involving WO_2Cl_2 are slightly endothermic, and they are favourable only due to the entropy factor of gaseous Cl_2 and O_2 (wherever applicable). It would therefore be interesting to attempt reactions of four chloride derivatives: AgCl, $AuCl_3$, and WO_2Cl_2 and CrO_2Cl_2 with the AgF_2 oxidizer.

2.2.7. Reactivity of AgF_2 with respect to oxides and chlorides: summary

The susceptibility of oxides, oxogenic salts, oxofluorides, chlorides, and oxochlorides, towards oxidation by AgF_2 as measured by the standard enthalpy of reaction, is illustrated in Fig. 5. Reactions with the smallest value of ΔH_r° have been considered for each compound.

2.2.8. Nitrides and nitrogen atom in N_2 and in amines

The relative susceptibility of oxides and chlorides towards AgF_2 suggests that all other simple inorganic ligands, which are softer than chloride and oxide (*i.e.* bromide, iodide, sulfide, selenide, telluride, nitride, phosphide, carbide, silicide) should

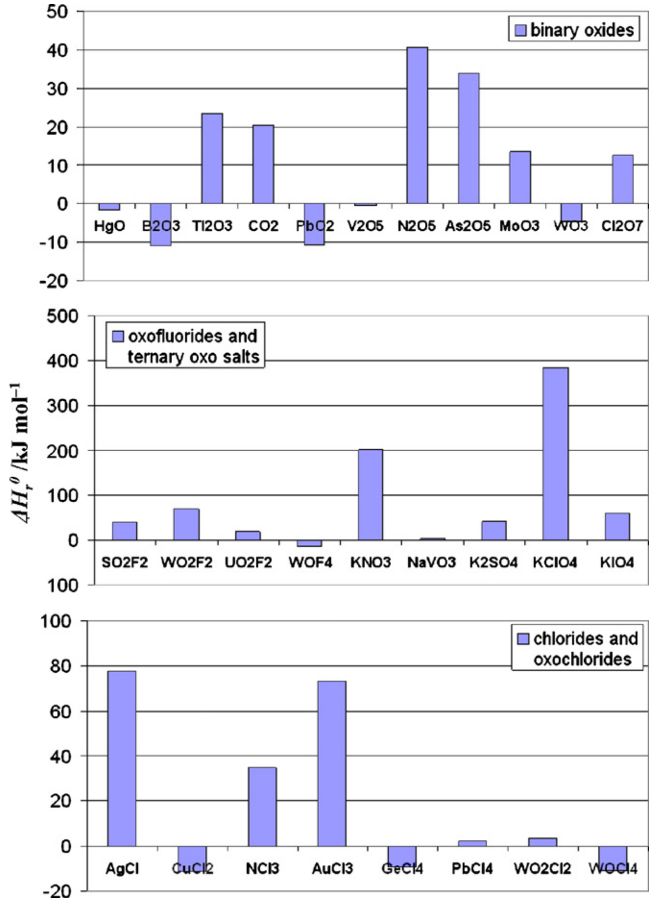


Fig. 5. Graphical representation of the standard enthalpy of reaction, ΔH_r° (kJ mol^{-1}), for the reactions of AgF_2 with a selection of binary and ternary oxides, chlorides, oxofluorides and oxochlorides. Reactions with the most negative value of ΔH_r° have been considered for each compound. Note different vertical scales for each graph.

be oxidized easily by AgF_2. This is exemplified by the case of lithium nitride:

$$(1/3)Li_3N + AgF_2 \rightarrow LiF + AgF + (1/6)N_2 \tag{9}$$

with the impressive standard enthalpy of this reaction of -406.7 kJ mol^{-1}. Importantly, N_2 itself should *not* be oxidized at ambient conditions by AgF_2 in the process:

$$(1/6)N_2 + AgF_2 \rightarrow AgF + (1/3)NF_3 \tag{10}$$

since the reaction enthalpy equals +111.4 kJ mol^{-1}, at the small entropy term of -25.7 kJ mol^{-1}.

One might consider using *perfluorinated* amines as ligands towards Ag^{II}. But will the C–N bond in organic matter resist fluorination? Unfortunately, thermodynamic data for the perfluorinated tertiary amines are not available in the literature. We are therefore forced to use the data for non-fluorinated amine, $(CH_3)_3N$, to get a rough estimate of the C–N bond's susceptibility to fluorination. The process:

$$(1/3)(CH_3)_3N_{(l)} + AgF_2 \rightarrow CH_3F_{(g)} + AgF + (1/6)N_{2(g)} \tag{11}$$

turns out to have a large positive reaction enthalpy of +92.5 kJ mol^{-1}, at the $-T\Delta S$ term of -55.5 kJ mol^{-1} (Eq. (11)) illustrates the fluorination of the C–N bonds *only*, so we do not consider here possible fluorination of the C–H bonds). Recollect, several compounds are known where Ag^{2+} is coordinated by non-fluorinated amines, such as pyridine, bipyridyl or tetraazamacrocyclic chelating ligand [8–10]. Since the F substituent exerts rather strong inductive effect (withdrawal of the electron density from the σ C–N bond and from the lone pair at N atom), it is expected that the C–N bond in fluorinated amines will be even less susceptible to fluorination by AgF_2 than the one found in non-fluorinated amine. A question remains open if the ability of perfluorinated amines (such as $(CF_3)_3N$ or tetrafluoropyridine) to coordinate Ag^{II} will suffice to form strong $N \rightarrow Ag^{II}$ bonds in extended solids. The beneficial energy of formation of these bonds should overcome a substantial part of the lattice energy of AgF_2 if the complex (for example $[AgL_2]F_2$ or $[AgL_4]F_2$, where L is an amino ligand) is to form.

2.3. Ag^{II} transfers the d^9 hole into the oxide and chloride bands

Why does Ag^{II} oxidize O^{2-} and Cl^- anions with such ease? The reason lies of course in the anomalously large value of the second ionization potential of Ag, and thus in an unusually low position of the d orbitals of Ag^{II} in the energy scale.

Moreno et al. was the first to note that an Ag^{II} impurity embedded in the host lattice made up from chlorides or bromides yields an unusual electronic effect: most of the spin density, originally coming from the transition metal cation, is in fact delocalized over its anionic coordination sphere [20]. More quantitative evidence was provided by Müller-Rösing et al. [4], who have theoretically studied AgX, AgX_2 and AgX_3 molecules in the gas phase (X = F...I). Their calculations reveal for example, that valence isomer $Ag^{II\bullet}(Cl^-)_2$ ($^2\Sigma_g$) is *not* the lowest energy minimum on the potential energy surface, with the $Ag^I(Cl_2^{-\bullet})$ ($^2\Pi_g$) electromer some 0.15 eV below. It is anticipated that analogous phenomenon should take place also for various oxo or hydroxo species of Ag^{II}. Indeed, as the DFT calculations for the [2 × AgO] system show, the planar C_{2h} dimer $(Ag^{II\bullet}O)_2$ is *not* a global energy minimum; it is outperformed by peroxide species, $Ag_2{}^IO_2$, and also by the disproportionated form, $[Ag^I...OAg^{III}O]$ (Fig. 6). Preference for the $Ag_2{}^IO_2$ form over the $(Ag^{II\bullet}O)_2$ one is strictly related to the ease of hole introduction by $Ag^{\bullet 2+}$ into the O 2p orbitals; in fact, nearly all spin density resides on O and not on Ag in $(Ag^{II\bullet}O)$ and in its dimer, and therefore these species are better written as $(Ag^IO^{\bullet 1-})$ and $(Ag^IO^{\bullet 1-})_2$, respectively.

Similar hole introduction to the oxide or chloride band is likely to take place for extended solids. Our DFT calculations for hypothetical perovskite-related tetragonal intergrowth compounds containing flat $[AgF_2]$ layers intercalated by various $M^{II}O$ or M^ICl layers, reproduce this unusual feature (Fig. 7). For example, spin density turns out to reside mainly on O centers in tetragonal $[BaO][AgF_2]$.

Combined results of the quantum mechanical calculations for molecular and extended oxo and chloro species [4] containing

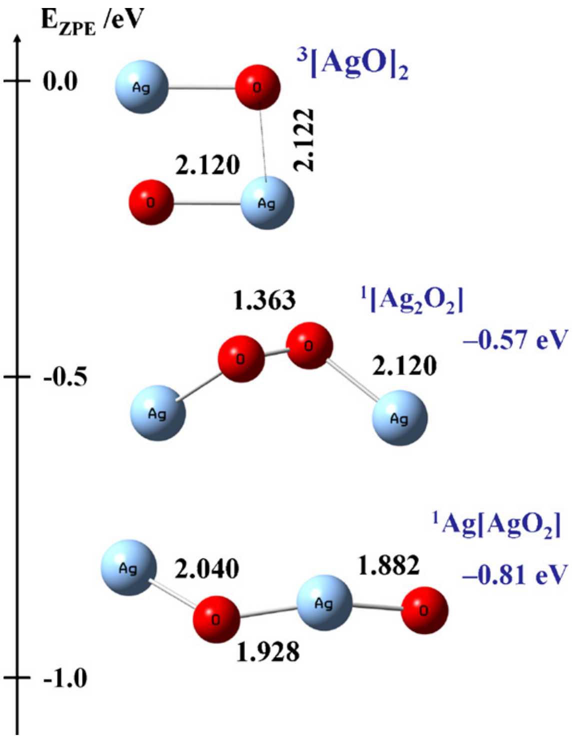


Fig. 6. Optimized geometries of three molecular species of the Ag_2O_2 stoichiometry: (A) $(Ag^{II\bullet}O)_2 \equiv (Ag^{I}O^{\bullet 1-})_2$ (C_{2h}), spin density resides mainly on O centers (0.95 e); (B) peroxide form $Ag_2{}^{I}O_2$ (C_2); (C) disproportionated form $[Ag^{I}\ldots OAg^{III}O]$ (C_1). The Ag–O bond lengths are in Å.

nominally Ag^{II}, suggest, that these species must be unstable with respect to oxidation of O^{2-} or Cl^{-} to $O_2{}^{2-}$ or Cl_2, respectively. The calculated energies of reactions (12)–(13) are quite negative:

$$[BaO][AgF_2] \rightarrow (1/2)BaO_2 + (1/2)BaF_2 + AgF \quad (-67.5\,kJ\,mol^{-1}), \tag{12}$$

and

$$[NaCl][AgF_2] \rightarrow (1/2)Cl_2 + NaF + AgF \quad (-22.2\,kJ\,mol^{-1}). \tag{13}$$

In conclusion, our calculations fully support the finding that oxide and chloride anions embedded in *ionic* solids cannot survive in the presence of the potent AgF_2 oxidizer. Scarce exceptions from this rule, discussed in the preceding sections, and summarized in Fig. 5, merit further experimental studies.

3. Conclusions

In this contribution we have analyzed thermodynamic parameters of various possible redox reactions between AgF_2 and many inorganic oxides, oxofluorides, chlorides and oxochlorides. Nearly all compounds in this group react exothermically with AgF_2 while releasing O_2 or, respectively, Cl_2. Only the binary compounds, HgO, CO_2, N_2O_5, V_2O_5, As_2O_5, SeO_3, MoO_3, WO_3, UO_3, Cl_2O_7, AgCl, $AuCl_3$, NCl_3, and $PbCl_4$, and a range of ternary compounds, nitrates, metavanadates, sulfates, chromates, perchlorates, MO_2F_2 (M = S, W), MOF_4 (M = W, U), and WO_2Cl_2, yield reactions which are either endothermic or have enthalpies very close to null. Since redox reactions considered here are connected with the evolution of gaseous products (O_2 or Cl_2), the entropy term of these reactions is usually negative, and the free enthalpy is positive only for a few oxo or chloro substrates. Hence, only an extremely limited number of oxides or chlorides could endure the presence of AgF_2 without being oxidized, as far as kinetics is not considered.

4. Computational methods

4.1. Thermochemistry

Majority of data have been taken from Ref. [15]. Only occasionally we have used data of the National Institute of Standards and Technology, USA (Chemistry Webbook at www.nist.gov) or an older data set [16] (for P_2O_5, PF_5 and POF_3; LaF_3; Tl_2O_3, TlF_3; InF_3; VOF_3; $GaCl_3$; WCl_6). For example, Ref. [16] gives the value of ΔH_f° of AgF_2 equal to $-347\,kJ\,mol^{-1}$. Therefore, at least a 13 $kJ\,mol^{-1}$ uncertainty applies to all ΔH_f° values listed in this work. All reactions

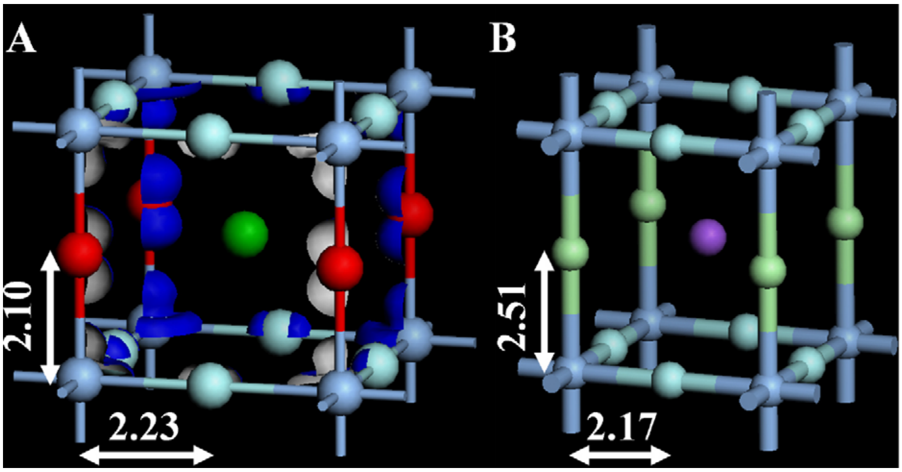


Fig. 7. Optimized unit cells of two hypothetical tetragonal compounds: (A) $[BaO][AgF_2]$ and (B) $[NaCl][AgF_2]$. The apical Ag–O (respectively, Ag–Cl) and horizontal Ag–F bond lengths are given in Å. Spin density, shown in blue for $[BaO][AgF_2]$ (isovalue of 0.025 e $Å^{-3}$), resides mainly on $O(2p_z)$ and $Ag(4dz^2)$ orbitals of the infinite [AgO] chains. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

considered involve reagents and products in their standard state at $T = 25$ °C and $p = 1$ bar, without any solvent.

4.2. Calculations for molecular $[AgO]_2$ systems

We used the B3LYP correlation-exchange functional, the 6-311++G* Pople basis set for O, and relativistic SDDAll pseudopotentials for Ag.

4.3. Calculations for extended systems

We have used the 600 eV cutoff, ca. $0.04 Å^{-1}$ k-point grid, 10^{-6} eV/atom SCF convergence, PBE correlation-exchange functional within the Generalized Gradient Approximation, and the ultrasoft Vanderbilt pseudopotentials.

Acknowledgements

WG thanks for support for this work from the Faculty of Chemistry and ICM UW, and from the national KBN grant (N204 167 32/4321). Author acknowledges the computational center in Warsaw (ICM) for providing access to the supercomputer resources and to the Gaussian'03 and Materials Studio packages. I would like to thank to Zoran Mazej (Ljubljana, Slovenia) for his valuable comments on this work.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2007.09.001.

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