Review

Strong Cationic Oxidizers: Thermal Decomposition, Electronic Structure and Magnetism of Their Compounds

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This work is dedicated to Professor Boris Žemva, the explorer of strong oxidizers par excellence.

Abstract

Strong oxidizers could be provisionally defined as compounds for which the standard redox potential exceeds 2.0 V in the NHE scale. Compounds which contain transition or post-transition metals at their unusually high positive oxidation states constitute one important family of strong oxidizers. Majority of such systems typically exhibit either diamagnetic or 'simple' paramagnetic properties down to very low temperatures. This is connected with the fact that highest oxidation states of metals are stabilized in fluoride environment and that binary high-valence metal fluorides form either molecular (0D) or low-dimensional (usually 1D) crystals. The ternary and higher fluorides are usually 0D in electronic sense leading again to low ordering temperatures. The situation becomes more interesting in selected compounds of Ag(II), the strongest oxidizer among all divalent cations, where one finds 2D or even 3D magnetic ordering at elevated temperatures. Thermal stability, electronic structure and magnetic properties of strong oxidizers are discussed jointly in this contribution with emphasis on the compounds of unique divalent silver.

Keywords: Electronic structure, fluorides, magnetism, oxides, oxidizer, silver

1. Introduction

One arbitrary definition of "strong" oxidizers might be that these are chemical compounds for which the standard redox potential, E^0, exceeds +2.0 V in the NHE scale.[1] Although this is quite a large fraction – close to a sixth – of the "textbook redox scale" (*ca.* –3.09 V to +3.05 V),[2] yet not many "strong" oxidizers are known. If we drop typical nonmetals and their compounds (F_2, O_3, OF_2, H_4XeO_6, XeO_3, $K_2S_2O_8$, $(SO_3F)_2$, $H_2N_2O_2$, etc. – which are usually diamagnetic even-electron systems), and fluorides of selected lanthanides at exotic tetravalent oxidation state,[3] as well as one actinide system,[4] we end up with about a dozen of cations of selected outer transition metals at the high(-est) oxidation states which may be contained in fluoride, oxide and (rarely) chloride systems (Figure 1, Table 1).

Several oxidizers even surpass the textbook +3.05 V limit (corresponding to the F_2,$2H^+$/2HF pair found in acidic environment) as exemplified by two classical $M(VI)F_6$ systems (M=Pt, Ir), $Ni(IV)F_4$[19] and $Ni(II)Ni(IV)F_6$[19]. These oxidizers are even stronger than KrF_2 and could be labeled as "ultra-strong" or "super-" oxidizers. Since $Ag(III)F_3$ has similar oxidizing properties as $Ni(IV)F_4$, the former species likely belongs in this family. Fluoride super-oxidizers are best obtained by the action of F radicals, which in turn are obtained via photochemical splitting of F_2 molecules. The E^0 value for the F^0,H^+/HF redox pair can be estimated at *ca.* +3.87 V (based on the corresponding value for the F_2,$2H^+$/2HF pair and the bond dissociation energy of F_2 molecule). The E^0 value for chlorine atom (radical) may be estimated in the same way at 2.62 V. The case of H_2O_2 confirms that such estimates are reasonable: the E^0 value for the OH°,H^+/H_2O pair obtained from the value for the H_2O_2,$2H^+$/$2H_2O$ pair[13] and the dissociation energy of the O–O bond[20] equals +2.85 V, while the experimental value is +2.73 V. *The redox potentials for the X°,H⁺/HX pairs (X=F, Cl, OH)* formally set the *up-*

Table 1. The values of the standard redox potential, E^0, for selected redox pairs where oxidizer contains metal cation at high oxidation state. The entries in bold fonts refer to benchmark systems containing nonmetals.[5]

Redox pair	E^0 [V]	Redox pair	E^0 [V]
$Pt(VI)F_6/PtF_6^-$	4.11[6*]	Cu(III)/Cu(II)	2.40[7]–2.30[8]
$F°,H^+/HF$	**3.87**[2]	$Au(III)F_3,H^+/Au(II),HF$	$XeF_2 < E^0 < F_2$
$Ni(IV)F_4/NiF_3$	> 3.8[9#]	$K_2Ni(IV)F_6/2KF, NiF_3$	$XeF_2 < E^0 < F_2$
$Ni(II,IV)F_3/NiF_2$	> 3.8[9#]	**XeF_2/Xe**	**2.32**[13]
$Ir(VI)F_6/IrF_6-$	3.61[6*]	$Pt(IV)F_4/PtF_2$	$< XeF_2$
KrF_2/Kr	**3.27**[10]	$Pd(IV)F_4/Pd(II,IV)F_3$	$< XeF_2$
$Ni(VI)O_4^{2-}/NiO_2$	3.12[11&#]	$Fe(VI)O_4^{2-}/Fe(III)$	2.20[12]
$Ag(III)F_3/Ag_3F_8$	$F_2 < E^0 < KrF_2$[@]	$Re(VI)Cl_6/ReCl_6-$	2.11[6]
$F_2,2H^+/2\ HF$	**3.053**[7]	$H_3Mn(V)O_4/MnO_2$	2.09[13,14,15]
$Os(VI)F_6/OsF_6-$	3.04[6]	**$O_3, 2H^+/O_2, H_2O$**	**2.075**[16]
$F_2/2F^-$	2.866[7]	$KPt(V)Cl_6/K_2PtCl_6$	2.06[6]
$Os(VI)Cl_6/OsCl_6-$	2.86[$]	$Pt(V)F_6-/PtF_6^{2-}$	2.06[6]
$Cl°,H^+/HCl$	**2.62**[2]	$Ag(III)O^+/Ag^{2+}$	2.016[17]
$Pb(IV)O_2/PbO$	2.47[13]	Ag^{2+}/Ag^+	1.98[13,18]
$KAg(III)F_4/KAgF_3$	$XeF_2 < E^0 < F_2$	$Pd(VI)O_3/PdO_2$	2.03[13]
$CsAu(V)F_6/CsAuF_4$	$XeF_2 < E^0 < KrF_2$	$Pt(VI)O_3/PtO_2$	2.00[13]
$Au(V)F_5/AuF_3$	$XeF_2 < E^0 < KrF_2$	$Cu(III)_2O_3,6H^+/2Cu^{2+},3H_2O$	2.00[7]

[*] estimated based on the value of electron affinity of MX_6 molecule in the gas phase; [&] at pH = 2; [$] theoretical value; $OsCl_6$ has not yet been prepared but its synthesis seems viable; [@] releases F_2 at room T; [#] formal potential.

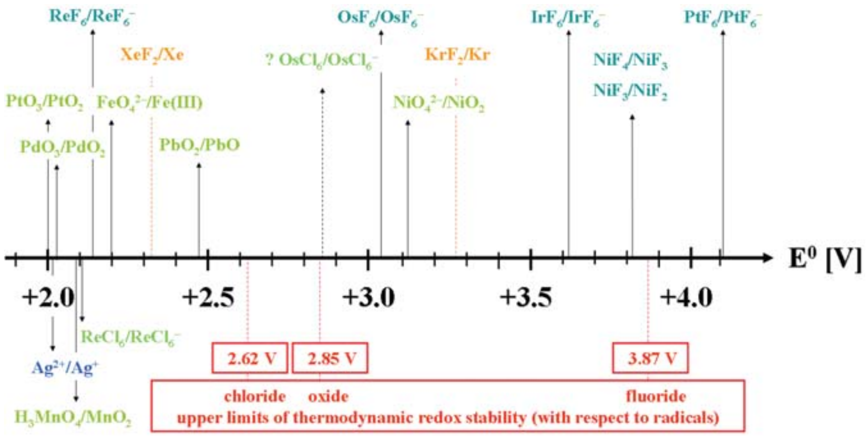

Figure 1. Illustration showing the selected redox pairs for which the standard redox potential, E^0, exceeds +2.0 V (cf. Table 1 and text). The upper limits of thermodynamic stability of X^- anions (X=Cl, OH, F) with respect to corresponding radicals, are provided.

per limits of thermodynamic stability of chemically bound X– anions with respect to loosing one electron (Fig.1).

The record E^0 value is set by the PtF_6/PtF_6^- redox pair and it was estimated to exceed +4 V; this result may seem surprising since PtF_6 does not spontaneously loose F radicals at ambient conditions. We will discuss this and similar cases later. The oxidizing properties can be strongly influenced by acidity of the environment. For example, AgF_3[21] and NiF_4 acidified in aHF with SbF_5 are capable of eliminating PtF_6 from its anion. Therefore, cationic forms (AgF_2^+ and NiF_3^+, respectively) seem to be more strongly oxidizing than PtF_6, but their neutral forms are likely the weaker oxidizers than PtF_6, etc. *AgF_2^+ and NiF_3^+ are currently the most potent oxidizers known to humans.*

The E^0 values for several important redox couples are not yet known but their lower and/or upper limits may – with some risk – be qualitatively estimated based on chemical reactivity of their oxidized forms. For example, the $Au(V)F_6^-$ salts may be obtained by action of KrF_2 oxidizer, so the redox potential of the anionic $Au(V)F_6^-/Au(III)F_4^-$ pair is certainly lower than the respective value for KrF_2/Kr system. On the other hand, the thermal decomposition of $KrF^+Au(V)F_6^-$ proceeds with elimination of Kr and formation of solid AuF_5, hence the E^0 value for the neutral $Au(V)F_5/Au(III)F_3$ pair must also be lower than the one for KrF_2/Kr. However, the $Au(V)F_6^-$ salts (as well as binary AuF_5) readily oxidize elemental Xe, hence their E^0 value must be higher than that of the XeF_2/Xe redox pair.

Presence of strong cationic oxidizers in the crystal structure of chemical compounds exerts strong effects on the properties of these compound, while affecting their electronic and magnetic structure, thermal stability and obviously chemical reactivity. The rule of a thumb is that the more strongly oxidizing the cation, the less thermodynamically and thermally stable are its connections with nonmetal-based ligands, and the stronger the d-p mixing in its electronic structure. The purpose of the current contribution is to focus on the impact of the presence of strong cationic oxidizers in chemical compounds on their magnetic properties from a joint perspective. Emphasis will be put on magnetic properties of the compounds of the unique Ag(II) oxidizer – the only divalent system capable of oxidizing elemental xenon while in its cationic form (AgF^+)[22] – and whose compounds show the most interesting magnetic properties of all compounds described here.

1. 1. Experimental and Computational Details

This paper means to serve as a critical compendium of data. Obviously, it is based in part on our previous experimental and theoretical work. The details of our experimental setup as well as of density functional theory (DFT) calculations have been described in several contributions, which will be evoked in the due course of this paper.

2. Results and Discussion

2. 1. Thermal Stability and Redox-reaction Triggered Decomposition of the Compounds Containing Strong Oxidizers

All strongly oxidizing cations (*cf.* Table 1) are ligated in chemical compounds by either fluoride, oxide or (more seldom) chloride anions. But stability of these connections for a given cation usually differs by a lot. Take tetravalent lead. PbF_4 is a colorless crystalline solid, which may be melted without decomposition at 600 °C. Related dark brown PbO_2 (note the colour – the electronic band gap must now be smaller!) is thermally unstable below 290 °C as it releases oxygen and transforms into Pb_3O_4. On the other hand, $PbCl_4$ is stable only below 0 °C as a liquid,[23] while related $PbBr_4$ and PbI_4 have never been reported. To further extend this series we might add that PbS_2 is known in both its $Pb(IV)(S^{2-})_2$ as well as $Pb(II)(S_2^{2-})$ forms (both are black) and thus the $Pb(IV)/Pb(II) – S_2^{2-}/2S^{2-}$ system is at the verge of the redox reaction, while related "$PbSe_2$" has only one polymorphic form, the $Pb(II)(Se_2^{2-})$ one showing the Se–Se bond. Thus, as far as the most electronegative ligands are concerned, the ranking of stability is: $F^{-1} > O^{-2} > Cl^{-1}$, followed by $S^{-2} > (Se^{-2}, Br^{-1}, I^{-1}, N^{-3}$ etc.).

Let us now take a look at thermal stability for a larger number of binary metal-nonmetal connections; we will discuss the emerging trends in stability of the binary metal-nonmetal connections, linking them to the behaviour of the chemical elements of the Periodic Table. For sake of simplicity we will focus on closed-shell cation/anion systems with the stable electronic configuration (octet) and we will see what is the propensity towards electron transfer between such "stable" cations and anions (*i.e.* breaking the octet) when the redox properties of the metal-nonmetal partners vary. To illustrate the crossover between "ionic" and "covalent" descriptions and concomitant redox destabilization this we have picked up sulphides of typical tetravalent elements of groups 4 and 14, MS_2 (M=Ti, Zr, Hf, Si, Ge, Sn, Pb, Ce, Th). The sulfides of moderately oxidizing species ($E^0 < 2V$) will thus serve us as an introduction to the chemistry of stronger oxidizers, for which less data exists in the literature.

2. 1. 1. Sulphides of Tetravalent Metals

Redox properties of tetravalent cations of elements from groups 4 and 14 vary from very weakly oxidizing (for M=Th, Hf, Zr), via moderately oxidizing (for M=Si, Ti, Ge, Sn) to quite oxidizing (for M=Pb, Ce) (Figure 2a). The limits of the E^0 value are set by Th^{4+}/Th^0 (–1.83 V) and Ce^{4+}/Ce^{3+} (+1.76 V) redox pairs. Accordingly, disulphides of all tetravalent elements except Pb and Ce adopt crystal structures which do not exhibit any marked S···S bonding contacts. Ionic formulation of $M^{4+}(S^{2-})_2$ might provisionally be assigned to this group of compounds. In contrast, disulphides of Pb and Ce are known in two polymorphic forms (Figure 2b). An ambient pressure form is similar to disulphides of other tetravalent elements and it shows no S···S bonding. However, the high-pressure (HP) forms (which can be quenched to ambient conditions) are different. HP–CeS_2 contains both the isolated sulphide (S^{2-}) and disulphide (S_2^{2-}) anions and it could be assigned the $Ce^{3+}(S^{2-})(S_2^{2-})_{0.5}$ formula. On the other hand, HP-PbS_2 contains exclusively the disulphide (S_2^{2-}) anions and it corresponds best to the $Pb^{2+}(S_2^{2-})$ description. Both HP forms of CeS_2 and PbS_2 are black and/or have metallic luster while testifying narrow or even closed band gap at the Fermi level. $Pb^{4+}(S^{2-})_2$ is is clearly metastable since it is reported to explode easily. Clearly, Ce^{4+} and Pb^{4+} oxidizers are capable of oxidizing the sulfide anions. The fact that two polymorphic forms are observed for each compound suggests that MS_2 stoichiometry is in each case at the verge of the redox reaction *i.e.* close to thermodynamic equilibrium. Closer inspection of the electronic structure, magnetism (in the case of CeS_2), transport properties and stability of these forms is worthwhile.

2. 1. 2. Chlorides

It seems that Pb(IV) is currently the most oxidizing cation to which chloride anion may be bound in the vici-

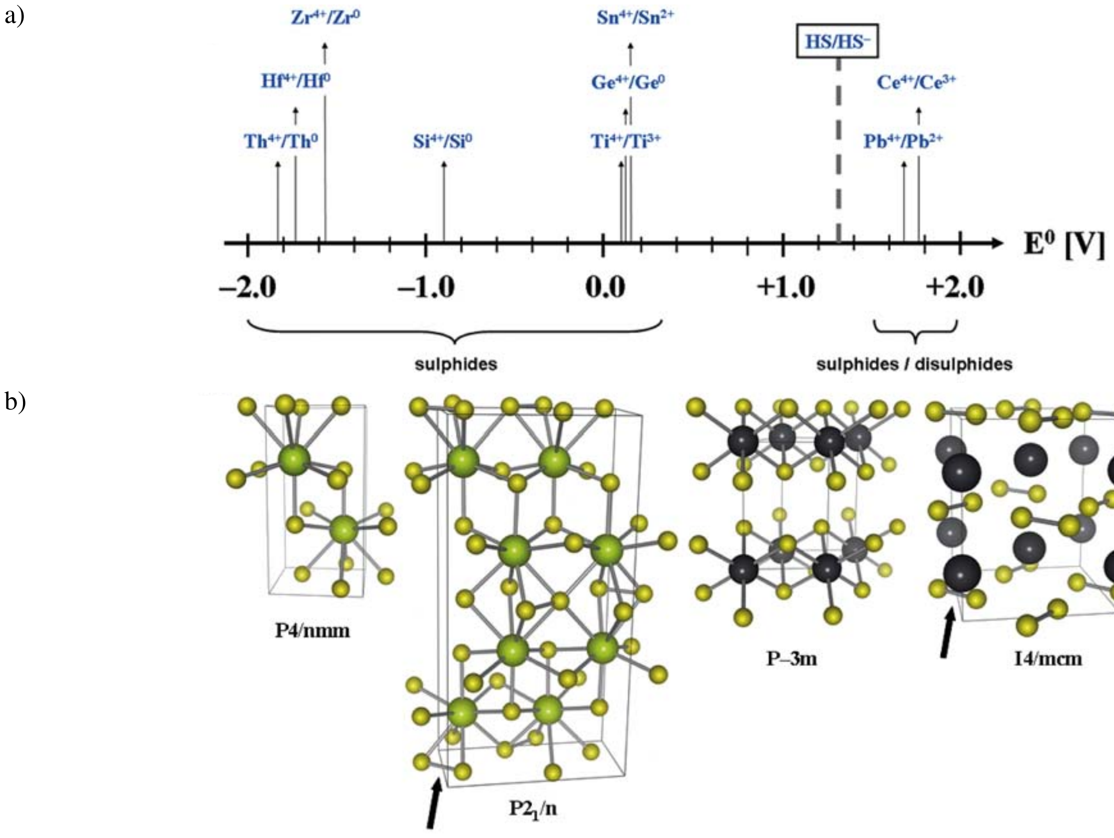

Figure 2. a) The values of the standard redox potentials for several closed-shell tetravalent cations. b) the crystal structures of two polymorphic forms of CeS_2 (left) and PbS_2 (right). Black arrows indicate the disulphide bonds with the short S–S contacts of 2.1–2.2 Å. Ce – large light, Pb – large black, S – small light balls. The approximate E^0 value for the HS/HS^- pair of +1.33 V has been indicated with broken line as based on the experimental data for organic RS radicals (the value for HS radical must be somewhat larger than that).[24]

nity of room temperature (the chlorides of Bi(V), Cr(V), Pt(VI), Pd(VI), Re(VI), Os(VI) and Ag(II) have not yet been prepared, while that of Xe(II) has been prepared only at very low temperatures in argon matrixes). It could be claimed that the upper limit of thermodynamic stability of chloride anion bound to strong oxidizer falls at +2.62 V *vs.* NHE, which correspond to the E^0 value for the Cl^0/Cl^- pair (the kinetic limit might be a bit larger than that). This offers some prospect for preparation of $AgCl_2$[25] (despite presumed lack of its thermodynamic stability at ambient conditions)[26] as well as a few other binary chlorides.

2. 1. 3. Oxides

Behaviour analogous to that of sulphides is observed also for oxides of the strongest cationic oxidizers. The main difference is that the E^0 values of cations needed to oxidize O^{2-} are much larger than those for the sulphides. For example, Ce^{4+} easily oxidizes S^{2-} anions. But pale yellow dioxide of Ce^{4+} (E^0 Ce^{4+}/Ce^{3+} 1.76 V), is very stable and it requires 690 °C in high vacuum to decompose.[27] Oxides of Bi^{5+} (E^0 Bi^{5+}/Bi^{3+} 2.0 V), Pb^{4+} (E^0 Pb^{4+}/Pb^{2+} 1.69 V) and Tl^{3+} (E^0 Tl^{3+}/Tl^+ 1.25 V) are all dark brown and they liberate O_2 only at increased temperature (Tl_2O_3 above 1000 °C,[28] PbO_2 above 290–300 °C,[29] Bi_2O_5 above 150 °C,[30]) while PoO_3 has so far been detected only in traces (despite a rather small E^0 for Po^{6+}/Po^{4+} of 1.51 V). Impressively, $Ru(VIII)O_4$ in the gas phase is kinetically stable even at 1275 °C and despite its thermodynamic instability.[31] Related colourless OsO_4 in the gas phase is also stable in this temperature range.[32] Red CrO_3 is stable in argon gas above its melting point and up to 270 °C,[33] but isoelectronic green Mn_2O_7 in the liquid state decomposes explosively even at room temperature.[34] Oxidation of oxide dianions thus requires quite potent oxidizers despite the act that dioxide anion in the gas phase is unstable with respect to electron detachment; for example black $Ni(IV)O_2$ decomposes exothermally above 120 °C,[35] black $Au(III)_2O_3$ above 150 °C[36] (alternative value: 264 °C[37]) while homologous $Ag(III)_2O_3$ showing shiny metallic luster is unstable with respect to elimination of O_2 even at room temperature.[38] For none of these stoichiometries is the alternative peroxide or oxide-peroxide formulation known.[39]

Unusual Ni(VI) in the claimed NiO_4^{2-} anion with its *formal* redox potential of *ca.* +3.1 V *vs.* NHE is the most oxidizing species claimed which formally contains oxide anions. In this case the thermodynamic limit of stability is possibly set by the experimental E^0 value for the related $[OH^{\bullet}$,

H^+/H_2O] pair at +2.73 V, so metastability of the NiO_4^{2-} anion reflects the presence of a kinetic barrier for breaking of the Ni-O bonds. Unfortunately, stable salts of this anion in the solid state (such as Cs_2NiO_4 or $BaNiO_4$) have never been prepared, and they constitute an interesting synthetic goal.

2. 1. 4. Fluorides

Obviously, fluoride anion is most stubbornly resisting oxidation among all anions. It is really difficult to thermally decompose fluorides with formation of elemental F_2. Mn(IV)F_4 constitutes a classical example of F_2-eliminating fluoride in preparative chemistry, even though Mn(IV) is not usually believed to be a very strong oxidizer. This is because most chemists' experience with limited oxidizing properties of Mn(IV) comes from their work with the oxide form, MnO_2. MnF_4 is much more potent oxidizer than MnO_2 and it is also thermally unstable. But majority of binary metal fluorides are very stable, even if metal is found at high (formal) oxidation state. Take PbF_4 which is a colorless crystalline solid, which may be melted without decomposition at 600 °C. AuF_3 which melts at 300 °C without decomposition, or BiF_5 which can be vapourized at 230 °C without elimination of F_2. PoF_6 and IF_7 are colorless and volatile solids, PtF_6 boils at 69 °C and IrF_6 at 53 °C without decomposition while TeF_6 is a thermally stable gas. Only three oxidation states of transition metals, Ag(III), Cu(III) and Ni(IV), are known to promote redox instability of the bound F^- anion at conditions close to ambient. In contact with aHF AgF_3 decomposes slowly at room temperature with the formation of Ag_3F_8,[21] various polymorphic forms of 'NiF_3' in the solid state *i.e.* Ni(II)Ni(IV)F_6 decompose thermally above 39–138 °C,[19] CuF_3 is unstable above –40 °C,[40] while the least thermally stable fluoride ever prepared, Ni(IV)F_4, looses fluorine above –60 °C.[19] AuF_7 – a purely hypothetical yet long sought species – in quantum mechanical calculations eliminates the F_2 molecule thus turning into $AuF_5 \cdots F_2$ complex.[41]

The E^0 value for the F^0/F^- redox pair can be estimated at *ca.* +3.87 V (which is clearly the most positive value among all anions); the values of E^0 for nearly all fluoride systems containing strong oxidizer fall below the "fluoride limit", except for PtF_6, which surpasses it by *ca.* 0.2 V. This feature reflects metastability of this molecule, and the presence of kinetic barrier for decomposition (*i.e.* detachment of F radical[42]). Another possibility is that the value suggested for the PtF_6/PtF_6^- pair has been overestimated.

2. 2. Electronic Structure of the Compounds Containing Strong Oxidizers

2. 2. 1. Molecular Systems

The ease of elimination of the oxidized form(s) of anions (*e.g.* Cl_2 or Cl° in the case of Cl^- anion) is obviously related to the electronic structure of species containing metal–nonmetal bond. This can be understood while analyzing the generalized potential energy surfaces (PES-s) for the ground state and the lowest among excited states of a molecule, the one which corresponds to breaking of the metal–nonmetal bond (Figure 3).

Take NaCl molecule. Its electronic ground state corresponds to a predominantly "ionic" description $Na^+ \cdots Cl^-$ (the wavefuntion o valence electrons is centered mostly on Cl) and the excited triplet state corresponding to a more-less atomic configuration $Na^{\circ} \cdots Cl^{\circ}$ is high in energy (Fig. 3a). The crossing of the "ionic" and "neutral" PESs takes place (since the first ionization potential of Na is larger than the first electron affinity of Cl) but only at very large metal–nonmetal separation of the order of 9 Å.[43] At such conditions an indeed dramatic redox process (*i.e.* Mulliken's "sudden electron transfer" or Polanyi's "harpooning effect") is very probable to occur; using the language of redox reactions this is *oxidation of* Cl^- *by* Na^+!

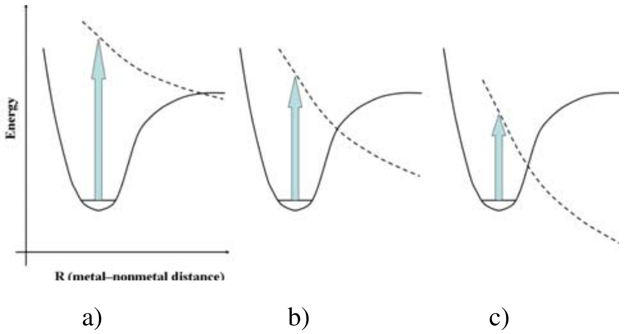

Figure 3. The generalized potential energy surfaces for the ground state and the lowest among excited states of a molecule, the one which corresponds to breaking of the metal–nonmetal bond. a) Ionic molecule which is very stable with respect to breaking of the metal–nonmetal bond via the redox reaction; b) moderately ionic molecule which is thermodynamically stable with respect to bond breaking but it exhibits pronounced mixing of the metal and nonmetal electronic states in both its ground state and the vertically excited state; c) covalent molecule which is thermodynamically unstable yet still kinetically metastable with respect to bond breaking. Vertical arrows stand for the ligand-to-metal charge-transfer (LMCT) optical transition.

As the oxidizing power of cation increases, the ionicity of the ground state decreases, the crossing of the "ionic" and "neutral" PESs takes place at shorter internuclear separations, and the energy of the ligand-to-metal charge-transfer (LMCT) optical transition decreases (Fig.3b); this may lead to a vivid colour of the compound, even if all of its constituents have a closed-shell electronic configuration. Although elimination of X° radical is not energetically favoured yet evolution o X_2 species may still be facile. This is because correct description of thermal decomposition usually requires an additional degree of freedom to describe the nonmetal–nonmetal bond formation (this may be alternatively viewed as a X–M–X bending coordinate, if molecule contains at least two X atoms at the M center). Coupling of X° radicals usually leads to substantial decrease of energy, hence compounds falling in category b) in Fig. 3 may be thermally unstable at ambient conditions. $PbCl_4$ is one good example; it readily liberates Cl_2 when heated above 0 °C.[23] $XeCl_2$ is another example – this compound may be stabilized only at low temperatures otherwise it dissociates to noble gas atoms and chlorine molecules.[44,45] The calculations of the PES of dissociation confirm that $XeCl_2$ is stable with respect to Xe + 2 Cl° but unstable with respect to Xe and Cl_2 (Fig. 3b).[46]

If cation is an even stronger oxidizer, "covalent" molecule becomes thermodynamically unstable with respect to elimination of X° radical(s) (Fig.3c). Radicals may be observed particularly at non-equilibrium conditions and at short timescale (they are eliminated but have no time to couple). Finally, when the excited state PES falls below what has so far constituted the ground state, molecule is unstable to redox process at any temperature.[47] This is exemplified by related $KrCl_2$ (obviously, the van der Waals cluster $Kr\cdots Cl_2$ constitutes the lowest energy configuration of this system)[48] or by $LiCl^+$ (note, divalent state of lithium is not achievable by chemical means). A hypothetical $PdCl_6$ also belongs in this category.[49]

It seems that quite a large number of strongly oxidizing systems could be metastable with respect to elimination of oxidized (radical) forms of anions. However, systematic screening of PESs for simple molecules which contain strong oxidizers is seldom performed. Usually, absolute energy of various nuclear configurations at various spin states is taken as a sufficient indicator of stability in theoretical studies.[50]

2. 2. 2. Extended Solids

If strong oxidizers form molecular solids, where molecules are weakly bound with each other via vand der Waals forces (PtF_6, KrF_2 etc.) analysis of their electronic structure and dissociation pathway may usually be limited to the "molecular" PES picture discussed in the previous section. However, if oxidizer forms an extended "polymeric" solid (*e.g.* 3D AgO, 2D AgF_2, 1D AgF_3) then the band structure / density of states description is more adequate. It will now be presented in a simplified form.

The classical picture of bonding in salts *i.e.* connections between metallic and nonmetallic elements is such that valence states of nonmetallic element are placed at higher binding energies and they are all occupied (octet), while the valence states of metal are found at lower binding energies and they could either be empty or partially occupied (Figure 4a). This *de facto* ionic picture comes from the fact that typical nonmetals are more electronegative than typical metals, so the states predominated by contribution from nonmetals lie at higher binding energies than those predominated by contribution from metals. This picture works fairly well or majority of transition metal and post-transition metal compounds, especially for the early transition metals; however, it is hardly applicable to the compounds of late transition metals and especially at their high oxidation states (*i.e.* strong oxidizers), as well as to the compounds of less electronegative nonmetals (such as phosphides, tellurides, arsenides, selenides etc.). In this case the very strong mixing is expected of the metal (cation) and ligand (anion) valence states, leading often to partial depopulation of valence orbitals of nometal ("holes" in the nonmetal states) (Figure 4b). At one extreme, the electronic states of metal cation may be placed at so large binding energy that the "inversion" of metal and nonmetal states might even take place[51] (Figure 4c). The states at the Fermi level of such "inverted" materials are usually predominated by contribution from nonmetal and they are labeled as "p metals" in solid state physics.[52] Elimination of nonmetal (or another type of oxidized form of its anions) from such compounds is facile.[53] Still, this effect is usually less pronounced than that for a related isolated molecule; solids consist of chemical bonds which are longer and more ionic than those in molecules due to (i) an increased coordination number of metal with respect to isolated molecule and (ii) a pronounced electrostatic (Madelung) stabilization which is absent for molecular monomers.[54]

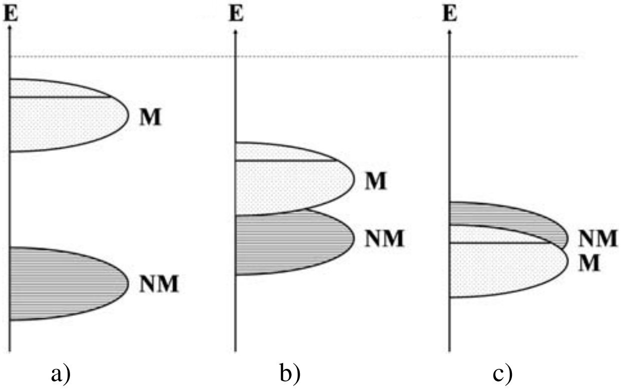

Figure 4. Schematic illustration of the mixing of metal (M) and nonmetal (NM) valence states in three types of chemical compounds: a) "ionic" compounds: the nonmetal valence states are occupied, those of a metal are empty, partially filled or filled depending on the electron count (horizontal line reflects the electron count), and there is small mixing between M/NM states; b) "covalent" compounds: there is substantial overlap between the metal and nonmetal valence states; the states of nonmetal may be partially depopulated; c) inversion of metal and nonmetal states in the energy scale; the valence states of nonmetal are highly depopulated and may predominate the states at the Fermi level; elimination of oxidized form of nonmetal anions is facile.

2. 2. 3. Examples: Theory

Let us now discuss several examples of interesting binary metal-nonmetal connections (both in molecular form as well as in the solid state) while focusing on their electronic structure. This will help us to understand uniqueness of strong oxidizers.

Molecular halides of silver in the gas phase (including the most interesting di- and trihalides) have been studied by Müller-Rösing *et al.*[55] It turns out that among molecular dihalides only the diluoride, AgF_2, can be described as a "normal" Ag(II) compound with the $^2\Sigma_g$ ground state. Already for $AgCl_2$ the $^2\Pi_g$ state is the minimum at linear geometry thus indicating the larger transfer of spin to the Cl centres. This is connected with the decrease of the charge on Ag from +1.09 e (for excited $^2\Sigma_g$ state) to +0.77 e (ground $^2\Pi_g$ state). The same situation takes place for AgX_2 (X=Br, I). The bent systems have not been studied,[55] but previous calculations by Rabilloud *et al.*[56] suggest the bent system as the ground state (Figure 5a). The short calculated Br···Br distance of < 3 Å is indicative of the partial Br–Br bonding, and suggesting the description as $Ag(I)(Br_2^-)$. Clearly, free spin shifts from Ag to Br. This has been confirmed by analysis of the occupied Molecular Orbitals (MOs), which resemble those of the isolated Br_2^- anion radical.[56]

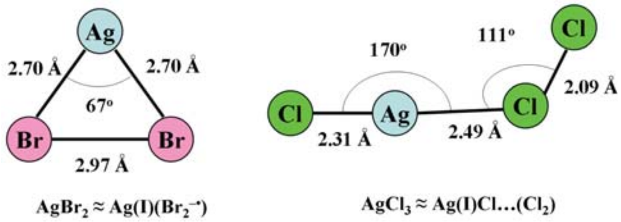

Figure 5. The calculated geometries of the $AgBr_2$ and $AgCl_3$ molecules in their respective ground states. Numerical data are taken from Refs. 55 and 56. One Ag(II) oxidizes one Br^- anion, while one Ag(III) oxidizes two Cl^- anions.

An even more dramatic electron transfer – this time involving two electrons – is predicted to take place for AgX_3 molecules when X=F is changed for Cl.[55] The T-shaped $^1A_1$ ground state of AgF_3 may be considered to contain genuine Ag(III). However, the L-shaped $^1A'$ ground state of $AgCl_3$ is in fact an adduct of Ag(I)Cl and Cl_2 molecules; the Cl_2 subunit show a very short Cl–Cl separation reminiscent of that found for the isolated Cl_2 molecule (Figure 5b). The $AgBr_3$ and AgI_3 species are similar to $AgCl_3$ in this aspect.

A hypothetical PdF_6 containing high-spin Pd(VI) ($4d^4$, distorted octahedron, triplet ground state) is another example where less unpaired electron density sits on metal center (0.65 e) than on six surrounding nonmetal atoms (1.34 e).[49] This must be reflected in relative content of atomic orbitals (AOs) of metal and nonmetal in molecular the MOs, but these features have not been analyzed by the authors. Regretfully, computational chemists dealing with isolated molecules are seldom interested in composition of molecular orbitals in terms of the atomic orbital basis (nice systematic studies of UO_2^{2+}, UON^+, UN_2 series,[57] as well as MO_2^{2+}, MN_2, and MP_2 where M = Mo, W[58] may be given as exceptions). Fortunately the case of solid state science is different and division of the density of states (DOS) to various atomic contributions (partial or atomic DOS) is a tool which is frequently used in analysis of chemical bonding for various families of compounds (and despite the fact that the frequently applied planewave basis sets functions are not centered on atoms).

To introduce methodology of analyzing properties of solid state compounds, we will focus here on the interesting family of difluorides[59] of coinage metals, MF_2 (M=Cu, Ag, Au).[60] These compounds differ a lot: colourless CuF_2 is a typical compound of copper at its most frequently found oxidation state, not much different from the corresponding chloride. On the other hand, dark brown AgF_2 is a very powerful – yet still thermodynamically stable – oxidizer; the corresponding chloride is unknown. Finally, related AuF_2 has never been prepared and it is very likely do disproportionate to Au(I) and Au(III) derivatives;[61] homologous $AuCl_2$ is in fact diamagnetic $Au(I)Au(III)Cl_4$.[62] The DOS for MF_2 (M=Cu, Ag) and for hypothetical AuF_2 optimized in the AgF_2-type structure, are shown in Figure 6.

With one unpaired electron per metal site fluorides of divalent coinage metals are expected to show magnetic ordering and band gap opening at the Fermi level. In our calculations we have not taken spin polarization into account, and the emerging band structure/DOS correspond to metallic

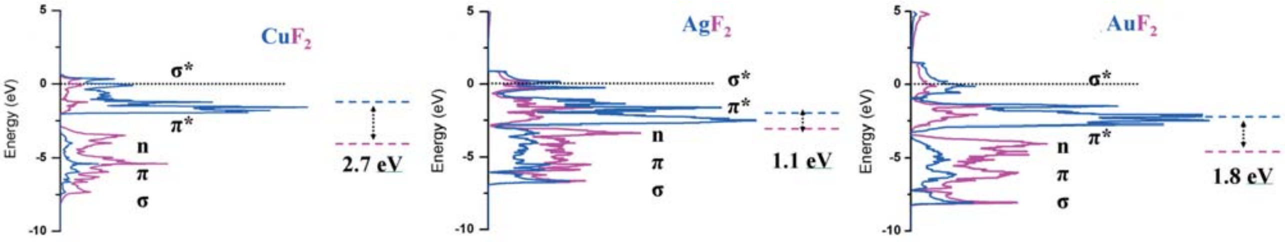

Figure 6. The calculated partial DOS for difluorides of coinage metals, MF_2 (M=Cu, Ag, Au) in the vicinity of the Fermi level. M(d) and F(p) contributions are shown in dark and light lines, respectively. Centers of gravity of M(d) and F(p) are indicated with dotted lines and their relative separation in eV is given. The absolute scale of DOS has not been given, as it is not essential to our considerations here.

compounds with a half-filled band. However, this simplified picture is sufficient for analysis of qualitative changes of chemical bonding in the MF_2 series as the transition metal is varied (we will introduce spin polarization to reproduce magnetic properties of AgF_2 and related compounds in section 3).

DOS for difluorides of coinage metals, MF_2 (M=Cu, Ag, Au) in the vicinity of the Fermi level may be divided in two sections: states at the larger binding energies predominated by contribution from F(2p) orbitals (these are mostly M-F bonding and non-bonding states) and the states at smaller binding energies predominated by the M(d) orbitals (mostly M-F antibonding states). CuF_2 (albeit some would disagree that it is ionic) is the closest to the definition of ionic compound among all MF_2 coinage metal systems: contribution of Cu(3d) states to the bonding states is small, and that of F(2p) to antibonding states is also small. But this changes dramatically for AgF_2: now the contribution of Ag(4d) states reaches up to nearly 50% in certain DOS regions (particularly these corresponding to σ bonding), so is the contribution of F(2p) to the antibonding states (for the highest energy σ* bands). In other words, Ag(II) markedly depopulates the stable octet configuration of F^- and AgF_2 is a strong oxidizer. The bonding picture for hypothetical AuF_2 again resembles that for CuF_2; this is due to relativistic effects which destabilize the 5d states and leads to smaller mixing of metal/nonmetal states than for AgF_2.

It is very useful to calculate the "center of gravity" of the M(d) and F(p) states, *i.e.* a weighted average of their energies with partial DOS values serving as a weight function;[63] these are indicated with dotted lines in Fig. 6 and their relative separation in eV is given. Clearly, the separation of the M(d) and F(p) states is the largest for Cu (2.7 eV) – this leads to their small mixing. Au is an intermediate case (1.8 eV), while for Ag the separation of the M(d) and F(p) states is the smallest (only 1.1 eV) – hence, their mixing is, consistently, most pronounced in this series.

Related hypothetical $AgCl_2$ in the solid state represents an unusual case of inversion of the center of gravity of the metal and nonmetal states.[25] Analysis of partial DOS indicates that Cl-dominant states are pushed as much as 1.9 eV *above* the Ag-dominant states and contribution of the former to bands at the Fermi level is slightly larger than that of the latter (!). Thus, nonmetal and metal states change their respective positions as we move from AgF_2 to $AgCl_2$ in the solid state. Remarkably, this is consistent with the behaviour of the related AgX_2 molecules (X=F, Cl) which adopt different electronic ground states and exhibit different occupations of metal–ligand bonding and antibonding orbitals.[55]

2. 2. 4. Examples: Experiment

A semi-quantitative insight into electronic structure of strong oxidizers may be gained for example from XPS spectroscopy. This is because the cross sections for interaction of different valence electrons with incident x-ray photon usually differ. This is especially true for 2p states of F and O which exhibit small cross sections as compared to majority of valence d (p) states of transition (respectively, post-transition) elements. For example, the Ag(4d) one-electron ionization cross-section of 2.1×10^{-2} Mb is over two orders of magnitude larger than the F(2p) one-electron ionization cross-section of 1.36×10^{-4} Mb under Al Kα excitation.[64] Thus, within the framework of the Gelius model[65] one anticipates that the experimental Al Kα XPS spectrum will be entirely dominated by the Ag(4d) contribution to the overall density-of-states profile. In other words, XPS analysis would be mapping mostly contribution of metal to various portions of the valence band.

Table 2. Ratio of the contributions of the Ag(4d) states to the "metal band" and to the "ligand band" for several silver fluorides (comparison of experimental and theoretical results). The integrated XPS area is presented here. Reproduced with permission from Ref. 66.

Species	Theory (DFT)	Experiment (XPS)
Ag(I)F	88:12	82:18
Ag(II)F_2	66:34	58:42
KAg(III)F_4	40:60	40:60

This feature has been used to analyze chemical bonding in a range of fluorides of silver, at oxidation states ranging from 1+ (mild oxidizer), via 2+ (strong oxidizer) to 3+ (very strong oxidizer) (Table 2).[66] It turns out that two broad bands are seen in the XPS spectra of AgF, AgF_2 and $KAgF_4$; the one at higher binding energies may be identified as the metal-ligand bonding states, while that at lower binding energies corresponds to the metal-ligand antibonding states.[67] We recall that in ionic compounds these are predominantly "ligand bands" and "metal bands", respectively. This is indeed the case of AgF where contribution from Ag(4d) states is seen mostly in the upper "metal band" in the XPS spectra (88%); only 12% of Ag(4d) go to the lower "ligand band" thus testifying to a rather small mixing of the Ag(4d) and F(2p) states within both bands. The situation changes for AgF_2, where already 34% of Ag(4d) states are found in the "ligand band". Remarkably, for $KAgF_4$ more Ag(4d) states go to the "ligand band" (60%) than to the "metal band" (40%); a similar feature has been observed in computations for this compound.[68] It clearly indicates that formulation of AgF_4^- ion as $Ag(III)(F^-)_4$ is very far from realistic; what is seen for $KAgF_4$ seems to be the first experimentally documented case of inversion of metal and nonmetal states in the energy scale.

Clearly, covalence of the Ag–F bonds increases in the order Ag(I) < Ag(II) < Ag(III) and it is significant in the fluorides of Ag(II) and Ag(III). The Ag(III) ion is an oxidizing agent of unprecedented power; concomitant with this covalence one sees the intrinsic property of holes being moved from Ag to F.

Although the XPS spectra were studied for a number o strong oxidizers such as $BaPbO_3$ and Ba_2PbO_4,[69] $NaCuO_2$,[70] PdO_3,[71] or $BaFeO_4$,[72] yet, regretfully, semi-quantitative analysis of chemical bonding similar to the one describe above are very seldom performed (see for example excellent work on PbO_2[73]).

Having analyzed thermal stability and electronic structure of strong oxidizers we now turn to their magnetic properties.

2. 3. Magnetic Properties of the Compounds Containing Strong Oxidizers

Magnetic interactions usually constitute a very small contribution to the internal energy of chemical compounds; nevertheless they have strong impact on the electronic properties such as band gap at the Fermi level, electronic conductivity, etc., and obviously on interaction with magnetic field. The 20 cations which are found in strong oxidizers (*cf.* Table 1) have in principle different d electron count – from d^1 to d^9 – and they show different number of unpaired electrons – from 0 to 4 (Table 3) – when found in a weak-field oxide or fluoride environment, chloride anions being a rarity. Occasionally, low spin configurations are observed for heavier transition metal compounds.

Table 3. The number of valence electrons, $n(e_{val})$, and the number of unpaired electrons, n(•), calculated assuming octahedral or tetrahedral environment, for selected highly oxidizing metal cations from Table 1 in their typical ligand environment (octahedral, square planar etc.). LS = low spin, HS = high spin.

Species	$n(e_{val})$	n(•)	Species	$n(e_{val})$	n(•)
Ag(II)	9	1	LS-Pt(V)	5	1
HS-Ni(II)*	8	2	LS-Pt(VI)	4	$0^{\&}$
HS-Ag(III)	8	2	HS-Ni(VI)$^{\#}$	4	4
LS-Ag(III)	8	0	LS-Ni(VI)$^{\#}$	4	2
LS-Cu(III)	8	0	LS-Pd(VI)	4	2
LS-Au(III)	8	0	Ir(VI)	3	3
HS-Ni(III)*	7	3	Mn(V)	2	2
LS-Au(V)	6	0	Os(VI)	2	2
LS-Pt(IV)	6	0	Fe(VI)	2	2
LS-Pd(IV)	6	0	Re(VI)	1	1
LS-Ni(IV)	6	0	Pb(IV)	0	0

* “NiF_3” contains predominantly Ni(III) but small amount of HS-Ni(II) and LS-Ni(IV) cannot be ruled out.[74] In M_3NiF_6 salts Ni(III) is mostly low-spin (n(•) = 1). $^{\#}$ spin state is unknown so both are considered here. $^{\&}$ See Ref.[76]

2. 3. 1. Overview of Magnetic Properties

Less than half of these cations have null number of unpaired electrons and their fluoride- or oxo- compounds usually exhibit diamagnetic properties. PtF_6 with a low spin Pt(VI) ($5d^4$) is an exception here as it is a van Vleck paramagnet.[75,76] Low lying excited states – likely with substantial charge transfer character – contribute to van Vleck paramagnetism of this compound. Obviously, there is strong mixing of the metal(d) and nonmetal(p) orbitals in the electronic structure of other compounds in this group, but since all electrons are paired up, there is not much to be excited about while analyzing at their magnetism.[77]

Great majority of compounds of the remaining oxidizers listed in Table 3 forms either molecular compounds (for example MF_6, M=Re, Ir, Os, or $(PtF_5)_4$) or ionic compounds where oxidizer is contained in anions in the lattice isolated from each other by magnetically inert cations (*e.g.* $K[AgF_4]$, $Cs_2K[AgF_6]$,[78] $Cs[AuF_6]$, $Rb[PtF_6]$, $K_2[NiF_6]$, $K_3[MnO_4]$,[79] or $K_2[FeO_4]$)[80]. All these compounds are paramagnetic; they may be considered as 0D in this sense that magnetic interactions are inherently weak and they may lead to some kind of magnetic order only at temperatures of the order of ~10 K and below; salts containing $Ni(VI)O_6^{2-}$ anion, if prepared, would likely fall into the same category. The constant Θ from the Curie–Weiss law, is occasionally larger (in terms of its absolute value); this happens for magnetically less dilute compounds with several unpaired electrons at one metal center – for example $BaFeO_4$ which exhibits Θ of –36.2 K.[80]

Binary fluorides at high oxidation states of a metal are, as we have seen, close to 0D magnets. The bonding situation becomes more interesting in oxides where – due to charge of (2–) on the oxide anion – one finds 2D and 3D networks even for high oxidation states of cations. This in principle could lad to magnetic ordering at elevated temperatures. The two sibling oxides, PdO_3[81] and PtO_3,[82] very likely show high dimensionality of the crystal lattice; regretfully, their crystal structures ad magnetic properties have never been determined. On the other hand, PbO_2 and its derivatives, $BaPbO_3$, Ba_2PbO_4, and the like, are diamagnetic; some are good conductors of electricity (*e.g.* $BaPbO_3$ is a semi-metal).[25,83]

Some compounds containing strongly oxidizing cations form infinite chains and thus they could be considered 1D also in magnetic sense; regretfully, most of them contain diamagnetic cations (*e.g.* $NaCuO_{4/2}$,[84] $AuF_{4+2/2}$, $AgF_{2+2/2}$[19]) so they do not give rise to spin ordering phenomena. The case of compounds of Ag(II) which contain 1D chains (for example $[AgF_{2/2}^{+}]$, $[Ag(SO_3CF_3)_{4/2}]$, or $[Ag(SO_4)_{2/2}]$ is unique and it will be described in a separate section. Two important 2D materials, AgF_2 and $Ag(SO_3F)_2$, will also be described together with other compounds of Ag(II).

As dimensionality (in sense of connectivity of crystal lattice via true chemical covalent bonds) increases, the magnetic properties usually become more complex – and more interesting. This is the case of three known crystallographic forms of ”NiF_3” for which in fact an alternative viable representation exists of a mixed valence Ni(II)/Ni(IV) fluoride.[19] The rhombohedral R-NiF_3 form is the most interesting case among the three polymorphic forms; it is a severely distorted variant of the ReO_3 lattice. R-NiF_3 consists of a primitive nearly cubic lattice of Ni(III) cations where each pair of cations is linked via fluoride bridge, with the Ni-F-Ni angle of *ca.* 138°. Although far from linear (180°), the fluoride bridge is still a host of antiferromagnetic (AFM) superexchange in 3D, which results in a departure from the Curie–Weiss law and field dependence of magnetic susceptibility below 250 K. A broad maximum of χ is seen at *ca.* 20 K for external field of 5 kG thus testifying to the presence of preeminent AFM interactions.[10]

The hexagonal form of NiF_3, H-NiF_3, exhibits a frustrated AFM ordering; the departure from the Curie–Weiss law and field dependence of magnetic susceptibility is seen below 120 K, with a broad maximum of χ at *ca.* 50 K detected at external field of 5 kG.[19] The pyrochlore form of NiF_3, P-NiF_3 (10% K^+ doped) also seems to be a frustrated AFM which obeys the Curie–Weiss law above 50 K. The paramagnetic Curie temperature, Θ, is positive though, and of the order of +20 K, indicating some spin canting which leads to "uncompensated" ferromagnetism.

2. 3. 2. Magnetism of the Compounds of Ag(II)

Divalent silver is unique species in the family of oxidizers, and this is for several reasons:

(i) it is the only divalent cation among strong oxidizers (Table 1), and the strongest oxidizer among all divalent metal cations;

(ii) due to the fact that formal charge on cation is small, Ag(II) may form polymeric compounds with mono- and doubly-charged anions and only seldom forms 0D molecular crystals;

(iii) electronic configuration of Ag(II) ($4d^9$) corresponds to one hole in the e_g set (σ^*) which leads to a pronounced Jahn–Teller effect and strong vibronic effects in general; this has impact on electronic, magnetic and optical properties of its compounds;

(iv) Ag(II) is a heavier congener of Cu(II) (cation which compounds are most studied of all transition metal cations)[85] yet compounds of Ag(II) are quite rare, and chemistry of its oxo-connections has been advanced only recently[86,87,88,89,90,91,92] very large exchange constants have been measured for some of them;

(v) the similarities between Ag(II) and Cu(II) and understanding 2D materials based on Ag(II) are important for attempts of synthesis of Ag(II)-based superconductors.[68,93]

Therefore, it seems sensible to devote a separate section to compounds of Ag(II).

Magnetic properties of fluorides, which constitute the largest family of the compounds of Ag(II), have been reviewed before[68] so only the most interesting ones will now be discussed.

Orthorhombic AgF_2 exhibits a layered structure with puckered [AgF_2] sheets (Ag–F bond lengths: 2.068–2.074 Å, Ag–F–Ag angles: 129.6°); the layers are interconnected with each other via longer Ag···F contacts of 2.584 Å.[94] The main components of the magnetic moments are parallel to *a* vector and they form a 2D (intra-sheet) antiferromagnetic structure; this results in huge and negative paramagnetic Θ constant of –715 K (–61.6 meV).[95] However, there is a non-vanishing spin component perpendicular to the sheets, which leads to a behaviour of AgF_2 as a spin-canted ferromagnet below 163 K (Figure 7 and Table 4). It is worthwhile to note, that AgF_2 exhibits the record strong 2D AFM interactions among all strong oxidizers. However, theoretical predictions suggest that its high pressure form, δ-AgF_2 exhibiting flat [AgF_2] sheets, could show even larger AFM interactions with intra-sheet coupling constants reaching –300 meV,[96] thus rivaling those measured for precursors of oxocuprate superconductors.[97]

α–K_2AgF_4[98], Rb_2AgF4[99] and Cs_2AgF_4[100,101] are derivatives of AgF_2 which can be synthesized by its reactions with alkali fluorides. These compounds are layered but not isostructural; α–K_2AgF_4 has a puckered-sheet while Cs_2AgF_4 a flat-sheet structure, and marked differences in bonding pattern exist between the two; structure of Rb_2AgF_4 awaits to be determined. All compounds in this series show 2D ferromagnetism with intra-sheet superexchange constant of the order of 5 meV (Table 4). Small distortions from the K_2NiF_4-type structure (I4/mmm) are responsible for the observed ferromagnetism.[93]

$Ag(SO_3F)_2$ is another important 2D material;[88] it is structurally related to AgF_2 and it exhibits puckered [$Ag(SO_3F)_2$] sheets. One possible synthetic pathway towards $Ag(SO_3F)_2$ is insertion of SO_3 into Ag–F bonds of AgF_2; interestingly, 2D character of a fluoride substrate is preserved in the product. However, the exchange pathway (Ag-O···O-Ag) is now more complex than that seen for AgF_2 (Ag-F-Ag) and one of the O-O-Ag angles is close to 90°, which results in intra-sheet magnetic exchange being ferromagnetic in type (Figure 7 and Table 4).

$Ag(pyz)_2(S_2O_8)$[102,103] (pyz = pyrazine) and $Ag(nic)_2$[92] (nic = nicotinate, *i.e.* pyridinecarboxylate) provide interesting examples of 2D compounds of Ag(II) with organic ligands equipped with N- (pyz) or N- and O- (nic) donors. These compounds no longer are "strong oxidizers" according to our provisional definition, since ligation with organic Lewis bases reduces the standard redox potential of the Ag(II)/Ag(I) pair by *ca.* 0.5 V. But they have interesting magnetism; the predominant intra-sheet exchange is AFM and still quite strong, given that superxchange extends over many atoms: from –4.6 to –5.7 meV for $Ag(pyz)_2(S_2O_8)$, from –2.4 to –2.6 meV for $Ag(nic)_2$. These values are much larger than those for rela-

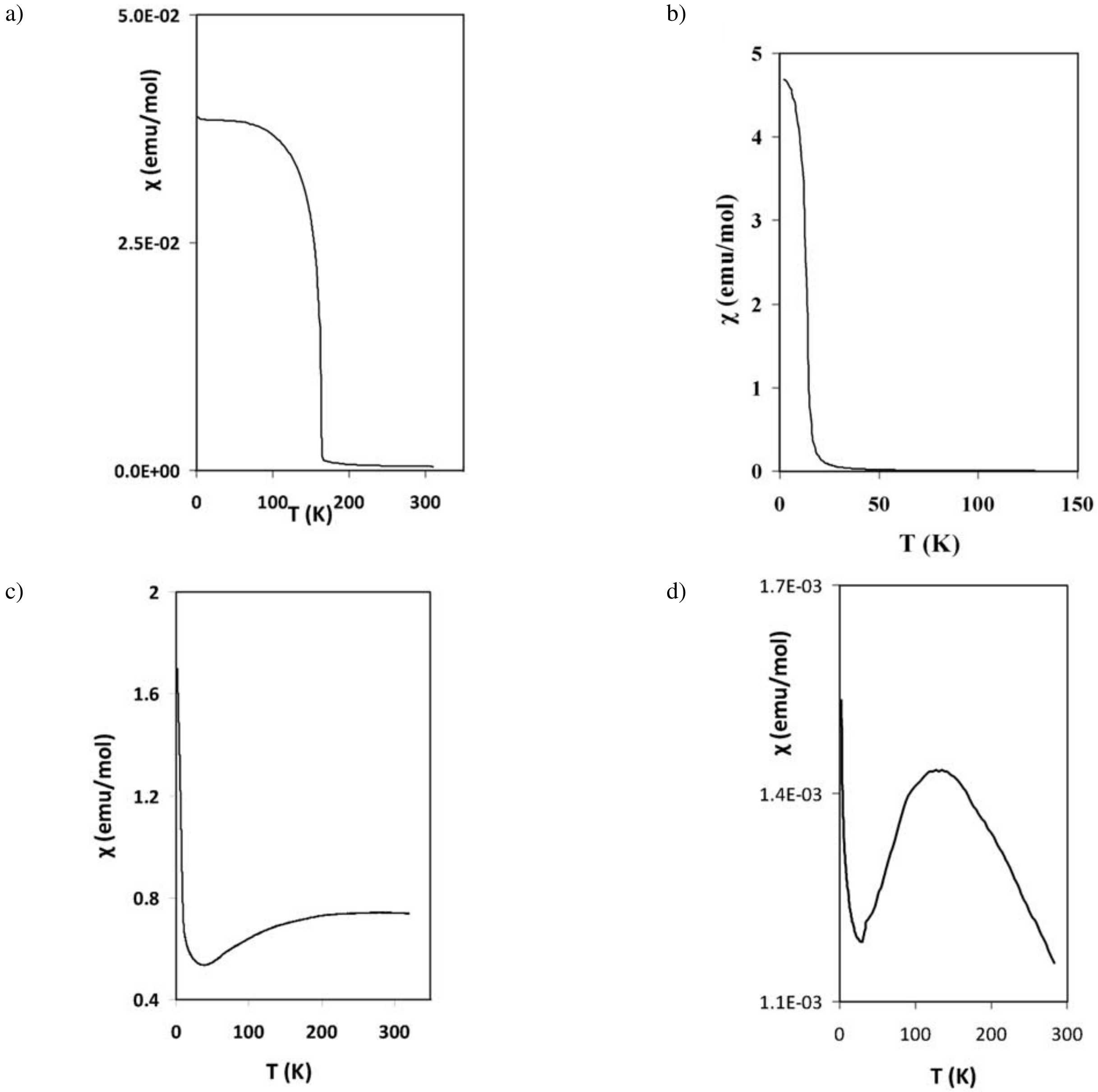

Figure 7. Magnetic susceptibility vs. temperature plots for a) AgF_2, b) $Ag(SO_3F)_2$, c) $AgSO_4$ and d) $Ag(SO_3CF_3)_2$. H = 1000 Oe.

ted Cu(II) salts, pointing out to a marked ability of Ag(II) for inducing spin polarization of the organic ligands. Log-range 3D ordering has been observed for $Ag(pyz)_2(S_2O_8)$ and $Ag(nic)_2$ below 7.8 K and 11.5 K, respectively. Attempts of chemically doping to $Ag(pyz)_2(S_2O_8)$ targeting to introduce mixed valence, have failed.[102]

The 1D materials based on Ag(II) may also exhibit appreciable magnetic superexchange. This is exemplified by $AgSO_4$, which exhibits the record strong 1D AFM interactions among all compounds of Ag(II).[87] $AgSO_4$ exhibits 1D spin fluctuations with susceptibility maximum of 285 K, and exchange constant of –217 K (–18.7 meV) (Figure 7 and Table 4).[104] This value is impressive, indeed, since AFM interactions between Ag(II) centers in $AgSO_4$ are due to super-superexchange involving the O···O bridge. Successful introduction of holes on O results also in facile thermal decomposition of this compound; the thermal decomposition temperature of *ca.* 100 °C is record low among all sulfates.[90] Magnetic interactions propagate along 1D $[Ag(SO_4)_{2/2}]$ infinite chains, although double $[Ag(SO_4)_{4/2}]^{2-}$ infinite chains (which support AFM exchange) are also present in the crystal structure.[105] Crystal structure of $AgSO_4$ resembles that of NaCl (fcc) in terms of cation-anion packing and therefore the AFM interactions in 3D are frustrated.[106] No definite proof of 3D magnetic order has been detected for $AgSO_4$ although a small maximum of susceptibility at 8.5 K has been occasionally observed or some samples.[106]

Table 4. The magnetic properties of selected compounds containing highly oxidizing metal cations from Table 3. pyz = pyrazine, nic = nicotinate, Dim. = structural dimensionality. ND = not determined, LT = low-temperature form.

Compound	Θ /K	T_{order} /K	μ (μ_B)	Dim.
Ag(II)F_2	< –715	163–165	ND	2D
Ag$(pyz)_2(S_2O_8)$	–66.8	49	ND	2D
Ag$(nic)_2$	–46.0	28.7	ND	2D
α–K_2AgF_4	+26	13	1.0	2D
$Ag(SO_3F)_2$	+24.8	24.8	1.08	2D
Cs_2AgF_4	+30	14.9	0.8	2D
Ag(II)SO_4	ND	285	ND	1D
[Ag(II)(SO_3F)][Ag(I)$_2(SO_3F)_3$]	ND	225	ND	1D
$Ag(SO_3CF_3)_2$	ND	140	ND	1D
[Ag(II)F]BF_4	*	?	ND	1D
$KAgF_3$–LT	ND	64	ND	1D
β–K_2AgF_4	1	5	ND	1D

* possibly a Pauli paramagnet (metal) above the ordering temperature

The mixed-valence $Ag_3(SO_3F)_4$ provides another example of a system with strong 1D AFM interactions (Table 4). This compound could be described in terms of magnetic exchange pathways as [Ag(II)(SO_3F)][Ag(I)$_2(SO_3F)_3$] with infinite [Ag(II)$(SO_3F)]^+$ chains responsible for the observed magnetic properties. $Ag_3(SO_3F)_4$ testifies that super-superexchange via O···O bridge of the SO_3F^- anion may be nearly as effective as the one for the related SO_4^{2-} anion.

$Ag(SO_3CF_3)_2$ *i.e.* silver(II) triflate, a sibling of $Ag(SO_3F)_2$, shows a markedly different magnetic behaviour from its congener (Figure 7 and Table 4). Instead of being 2D FM, $Ag(SO_3CF_3)_2$ is a 1D AFM, with exchange pathway along the $[Ag(SO_3CF_3)_{4/2}]$ infinite 1D chains. Ag(II) cations are linked via two anions within the chain; recall, similar double $[Ag(SO_4)_{4/2}]^{2-}$ chains are seen for $AgSO_4$.

Fluorides of Ag(II) may also exhibit strongly anisotropic 1D magnetic properties. This takes place for $KAgF_3$,[98] which – despite its distorted perovskite structure – consists of a network of short Ag–F bonds arranged into a 1D $[AgF_{2/2}{}^+]$ infinite chain. Magnetic interactions along the chain result in a moderately large ordering temperature of 64 K; however, it cannot be excluded that this value corresponds to 3D ordering, while characteristic temperature associated with 1D fluctuations of spins is one order of magnitude larger. The case of related $AgFBF_4$ and several other AgF^+ salts[107] which exhibits well-defined straight or kinked $[AgF_{2/2}{}^+]$ infinite chains, and were claimed to be Pauli paramagnets (metals). For example, χ for $AgFBF_4 = 1.8 \times 10^{-4}$ emu/mol. These salts show interesting anomalies of susceptibility when washed with aHF and their magnetic properties certainly require careful reinvestigation.

Superexchange between Ag(II) centers may also be transmitted via a double fluoride bridge, as it occurs for β–K_2AgF_4.[108] However, since long-short Ag–F–Ag bonding patterns are present within these chains, the resulting superexchange is small, and leads to Θ of the order of 1 K. The symmetric $[AgF_{4/2}]$ double chains analogous to those seen for $Ag(SO_3CF_3)_2$ with only short Ag–F bonds have not been seen yet in any fluoride of Ag(II).

As follows from this overview, the spectrum of possible super(-super) exchange pathways involving F, O and even N and C atoms is thus very rich and leads to diverse values of exchange constants in compounds of Ag(II).

3. Conclusions

In summary, we have described here fundamental properties of the compounds of strong oxidizers ($E^0 > 2$ V *vs.* NHE) such as their redox properties, thermal stability, electronic structure and magnetism. We have focused on systems which contain transition or post-transition metals at their unusually high positive oxidation states; with very few exceptions these are fluoride or oxide systems.

We have identified set of features typical of strong oxidizers in the solid state which contain metal cations and nonmetal-based anions:

(i) binary high-valence metal salts form either molecular (0D, van der Waals) or low-dimensional (usually 1D) crystals; low dimensional character is more often found for fluorides; selected compounds of Ni(III) and Ag(II) (*e.g.* AgF_2) constitute important exceptions; oxide systems usually have higher electronic dimensionality (*e.g.* PbO_2);

(ii) ternary systems are usually 0D in electronic sense and they contain isolated anions with a central strongly oxidizing metal cation; polymeric systems are rare; again, compounds of Ag(II) provide exceptions from this rule, with diverse systems known of increased dimensionality (AgF^+, AgF_3^- and AgF_4^{2-} salts);

(iii) thermal stability of solid state systems is usually low, especially for oxide derivatives; decomposition proceeds via redox reaction (elimination o the oxidized form of nonmetal anion); $AgSO_4$ has the lowest value of the thermal decomposition temperatue among all sulfates;

(iv) strong oxidizers exhibit very strong mixing of valence states of metal and of nonmetal which in rare cases may be inverted in the energy scale (*e.g.* $KAgF_4$);

(v) they may be coloured (due to charge-transfer ligand-to-metal transitions) even if the transition or post-transition metal center has a closed shell electronic configuration (*e.g.* PbO_2);

(vi) magnetic interactions – if free spins at metal centers are present – are usually weak for 0D systems; majority of such systems typically exhibit either diamagnetic or 'simple' paramagnetic properties down to very low temperatures;

(vii) compounds of Ni(III) and Ag(II) are exceptional in this sense that very strong magnetic superexchange often takes place for polymeric (1D, 2D or 3D) systems. AgSO$_4$ holds the record of the super-super exchange constant (via O…O) bridge between metal centers, despite the fact that only one unpaired electron per metal center is available.

As follows from i), ii), iii), and vii), Ag(II), the most powerful oxidizer among all divalent cations, is really unique species in the family of strong oxidizers.

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5. References

1. In this case the expression "very strong" oxidizers could be reserved for systems for which the E^0 value exceeds +3.0 V *vs.* NHE.
2. The textbook range is from about –3.09 V for H$^+$, 3/2 N$_2$/HN$_3$ to about +3.05 V for F$_2$, 2H$^+$/2HF. There is one important exception falling outside the standard range, namely a fluorine radical (atom).
3. Dy^{4+}/Dy^{3+} +5.7 V, Nd^{4+}/Nd^{3+} +4.9 V, Pr^{4+}/Pr^{3+} +3.2 V, Tb^{4+}/Tb^{3+} +3.1 V.
4. Np(VII)O$_3^+$/NpO$_2^{2+}$ 2.04 V. Regretfully, the E^0 values for the highest oxidation states of Pu (VII, VI) in acidic environment are not available; also, it is not unreasonable that Pu(VIII)O$_4$ could exist.
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Povzetek

Močne oksidante lahko definiramo kot spojine, za katere standardni redoks potencial presega 2,0 V v NHE lestvici. Spojine, ki vsebujejo kovine v njihovih neobičajno visokih pozitivnih oksidacijskih stanjih predstavljajo pomembno družino močnih oksidantov. V večini takšnih sistemov najdemo bodisi diamagnetne ali »preproste« paramagnetne lastnosti, ki se izražajo do zelo nizkih temperatur. To je povezano z dejstvom, da so najvišja oksidacijska stanja kovin stabilizirana v fluoridnem okolju in da so binarni fluoridi v visokih oksidacijski stanjih bodisi v molekularnih (0D) ali nizko-dimenzionalni (običajno 1D) kristali. Položaj postane bolj zanimiv v izbranih spojinah Ag (II), ki je najmočnejši oksidant med vsemi dvovalentnimi kationi, kjer najdemo 2D ali celo 3D magnetno urejanje pri višjih temperaturah. Termična stabilnost, elektronska struktura in magnetne lastnosti močnih oksidantov so v prispevku obravnavane skupaj, s poudarkom na spojinah dvovalentnega srebra.