

Review



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[†]This work is dedicated to Prof. Peter P. Edwards at his 65th birthday.

Chemistry of silver(II): a cornucopia of peculiarities[†]

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Silver is the heavier congener of copper in the Periodic Table, but the chemistry of these two elements is very different. While Cu(II) is the most common cationic form of copper, Ag(II) is rare and its compounds exhibit a broad range of peculiar physico-chemical properties. These include, but are not limited to: (i) uncommon oxidizing properties, (ii) unprecedented large mixing of metal and ligand valence orbitals, (iii) strong spin-polarization of neighbouring ligands, (iv) record large magnetic superexchange constants, (v) ease of thermal decomposition of its salts with O-, N- or C-ligands, as well as (vi) robust Jahn–Teller effect which is preserved even at high pressure. These intriguing features of the compounds of Ag(II) will be discussed here together with (vii) a possibility of electromerism (electronic tautomerism) for a certain class of Ag(II) salts.

1. Coinage metals: all different!

Copper, silver and gold rank among a few chemical elements that have been known to human beings for millennia. They are quite abundant in the Earth's crust (particularly Cu¹) and they have humbly served humanity over the last 7500 years, notably in the development of tools and weapons in the chalcolithic (Cu) and bronze (Cu–Zn–Sn alloys) periods, and later in establishment of the fiscal system (Au and Ag). Dropping of the gold standard (e.g. in 1931 by Great Britain) and

¹Atomic abundance: 22 000 ppb Cu, 20 ppb Ag, 0.3 ppb Au, which corresponds roughly to 100 000:100:1. The numbers of crystallographically characterized compounds of these elements are 61 242, 16 049 and 9701, respectively, their ratio being close to 6:2:1. The statistics are based on CSD and ICSD crystallographic databases (accessed 6 May 2014). The typical ratio of the number of organic to the number of inorganic compounds is three to four for each coinage metal.



Figure 1. Native copper, silver and gold, with their alchemical symbols above each element, as well as a miscibility triangle showing colours of diverse Cu–Ag–Au alloys.

the issuing of ‘*fiat* currencies’ which followed have been often held responsible for major economic crises of the twentieth and twenty-first centuries. All three elements have been vital in alchemists’ holistic view of Nature (figure 1) and—since they are miscible with one another in all proportions—they have been used for crafting jewellery. All of them occur in the free state in Nature (figure 1), and Cu in Ag are found in ores, as well.

Element 111, roentgenium, joined the metallic triad in December 1994, when it was synthesized for the first time [1]; with its minute amount synthesized in a very costly experiment it is certainly more precious than gold, and it turns out it is more noble, as well [2]. Its calculated ionization potential of 10.6 eV is larger than that of gold (9.2 eV), so it will form cations with more difficulty. Simultaneously, its calculated electron affinity of 1.56 eV is smaller than that of gold (2.31 eV), which points to the weaker electron-acceptor properties and thus less ‘non-metallic’ nature of roentgenium when compared with gold. Again, Rg proves to be the less reactive of the two.² Moreover, Rg has been predicted to adopt an uncommon electronic configuration of its atom in the ground state: $[\text{Ng}](N-1)d^9(N-2)s^2$, as contrasted to those taken by its three lighter siblings: $[\text{Ng}](N-1)d^{10}(N-2)s^1$ [1]. This comes obviously from the strong impact of relativistic effects on the properties of heavy elements, and in particular from the progressive stabilization of the *s* orbitals and destabilization of the *d* ones across the series: Cu, Ag, Au, Rg. However, since Rg does not fall into the ‘coinage metal’ category for its short-lived nature as well as strong radioactive emission, we will omit this element from further analyses presented in this account.

2. Redox–redux

As argued by Pyykkö [3] and others, only silver is a ‘normal’ transition metal of the triad. This is (partly) due to nodeless nature of the $3d$ orbital of Cu, the relativistic features of Au and the very modest impact of relativistic effects on properties of Ag.

Indeed, silver metal is ‘silverish’ just like all other transition metals—except copper (‘red’) and gold (‘yellow’). Progressive addition of silver to either copper or gold renders the latter metals less intensely coloured (figure 1). But there are major differences in many more physical and chemical properties of these elements, as well. Of particular interest here are the redox (electron-transfer) properties. Cu(II) is the most frequently found oxidation state of this element, largely due to large solvation energies of this small cation, which partly counterbalance the energy required to ionize Cu(I) by one electron. By the same argument, atoms of ‘normal’ silver are larger than those of copper, and thus this element prefers to adopt the first oxidation state. On the other hand, owing to relativistic effects, gold most frequently adopts the third oxidation state; interestingly, some

²This is also reflected in Mulliken electronegativity (χ_M) and Pearson hardness (η_P) of Au and Rg atoms: $\chi_M = 6.08$ eV (Rg) and 5.75 eV (Au), while $\eta_P = 4.52$ eV (Rg) and 3.45 eV (Au). Larger value of χ_M reflects stronger binding of electrons to the core, while larger value of η_P indicates smaller propensity of an atom to undergo chemical reactions.



Figure 2. Progress of reaction between AgF_2 (dark brown, in the glass container) and SiCl_4 (colourless, not seen, added dropwise from the top) carried out in an argon atmosphere.

binary compounds of Au(I) are still elusive, including prototypical AuF [4,5], since they exhibit strong tendency to disproportionate to $\text{Au}(0)$ and $\text{Au}(\text{III})$ compounds. Similarly, CuF has not been prepared in the condensed phase, and its synthesis still represents a challenge in contemporary synthetic chemistry [6,7].

The second oxidation state of silver is thus uncommon as it implies the destruction of the quasi-closed shell d^{10} electronic configuration of the $\text{Ag}(\text{I})$ cation (this feature is obviously expected for the ‘normal’ Group 11 element). With some effort, introducing one hole to the d shell of Ag may be realized; yet the resulting highly electron-deficient $\text{Ag}(\text{II})$ cation *claims its electron back* both in the gas phase [8] and when present in chemical compounds [9,10]. In other words, all species containing $\text{Ag}(\text{II})$ are very strong oxidizers. This feature is seen in the second ionization potential of silver being the largest of the three congeners ($21.45 \text{ Ag} > 20.52 \text{ Au} > 20.29 \text{ eV Cu}$); in fact, it is larger even than those of non-metallic P, Se or Xe, and very close to that of bromine (21.80 eV), a halogen! Concomitantly, $\text{Ag}(\text{II})$ is found mostly in fluoride ligand environments [11], and only in a handful of known compounds does its first coordination sphere contain O, N, C or S (see [12] and references therein). $\text{Ag}(\text{II})$ is incompatible with many common inorganic and organic anionic ligands such as iodides, bromides, chlorides, sulfides, cyanides, carbonates, amides, imides, phosphates, carboxylates, alcoholates, etc., and also with many neutral ones. Even covalently bound Cl atoms are targets of $\text{Ag}(\text{II})$ ’s attack; for example, AgF_2 fiercely oxidizes SiCl_4 at room temperature while breaking the Si–Cl bonds (figure 2) [10]. The C–Cl bonds also undergo rupture [9].

When $\text{Ag}(\text{II})$ cations are found in superacidic environments, and in the presence of weakly coordinating anions, they exhibit superb oxidizing properties. This is exemplified by AgF^+ cations solvated by anhydrous HF acidified with Lewis acids; these species are capable of oxidizing, *inter alia*, xenon and O_2 while yielding $\text{Xe}(\text{II})$ and O_2^+ cations, respectively [13]. Since both the first ionization potential of an O_2 molecule and that of a Xe atom exceed 12 eV , $\text{Ag}(\text{II})$ cations retain in this electron-deficient environment substantial share (approx. 50%) of their immense electron affinity in the gas phase ($E_A = 21.45 \text{ eV}$). Strongly oxidizing properties of $\text{Ag}(\text{II})$ are revealed also in the appreciable standard redox potential (E^0) for the $\text{Ag}(\text{II})/\text{Ag}(\text{I})$ redox pair which is close to $+2 \text{ V}$ versus normal hydrogen electrode (NHE) ($+1.98 \text{ V}$ [14]). This value formally corresponds to an aqueous environment albeit $\text{Ag}(\text{II})$ obviously oxidizes water, with O_2 and even some ozone, O_3 , as the products. The value of the formal redox potential (E^0) may be increased to as large as $+2.90 \text{ V}$ versus NHE for the $\text{Ag}(\text{II})$ species solvated in 30% oleum ($\text{H}_2\text{SO}_4 + \text{SO}_3$) [15,16]. This system seems to be the *strongest fluorine-free oxidizer* currently known. Some interesting electrochemistry with $\text{Ag}(\text{II})$ as electron-transfer species has been done in the past [17]; the practical use of the recently prepared $\text{Ag}(\text{II})$ /oleum system is currently under scrutiny.

3. Orbitals: mix them, mix them not

The large electron affinity of $\text{Ag}(\text{II})$ implies that the highest unoccupied valence $4d$ orbital of this species (the half-filled one) has a very large binding energy with respect to energy of an electron in

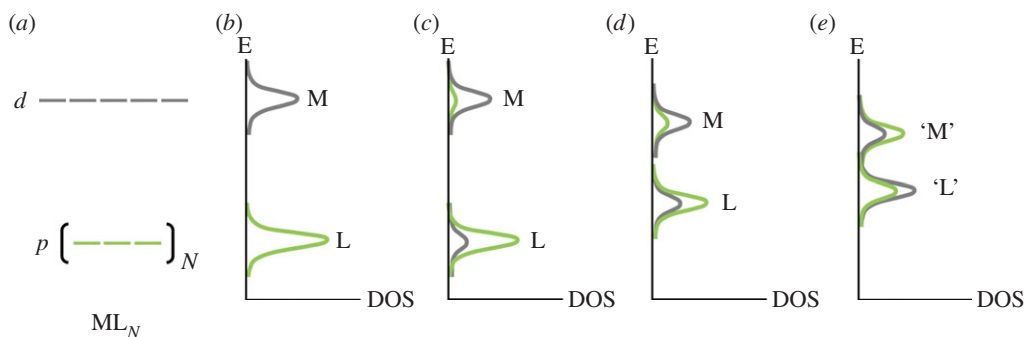


Figure 3. Schematic of the valence orbital mixing in transition metal–ligand complex or solid, ML_N . (a) The starting atomic basis set composed of five d orbitals of M cation and N times three p orbitals of non-metal anion (assuming monoatomic ligand for simplicity). (b) The corresponding picture in the DOS versus energy (E), assuming 100% ionic bonding. (c) A more realistic picture of bonding, assuming small admixture of ligand states to the top ‘metal band’ (M) and small admixture of metal states to the bottom ‘ligand band’ (L). (d) As before, but now at the increased oxidizing character of a metal cation, and/or increased reducing character of the ligand anion; there is more orbital mixing. (e) As before, but now the inversion of the metal and ligand states takes place and metal d orbitals contribute more partial DOS to the ‘L’ band than to the initial ‘M’ band.

vacuum. This must lead to substantial mixing of the metal and ligand valence orbitals in chemical compounds, since free anions (if stable in the gas phase!) usually exhibit small electron binding energies. The chemical potentials of cation and anion(s) of course become equal upon formation of a neutral chemical compound in the solid state (as anion forms donative bonding to cations, and some charge transfer takes place), yet the valence orbital mixing should still be very large in corresponding solids. This indeed proves to be the case, as we will discuss below.

Using the ramifications of the molecular orbital theory, one often constructs the molecular (or crystal) orbitals of a transition metal–ligand complex (or solid), ML_N , from the atomic orbitals of its elemental constituents (figure 3). The starting atomic basis set is composed of five d orbitals of M cation and N times three p orbitals of non-metal anion (assuming monoatomic ligand for simplicity). Assuming that the bonding is 100% ionic, the corresponding picture in the density of states (DOS) versus energy is such that electronic DOS is composed of a set of filled bands of a higher electron binding energy (local peak of DOS) which originate purely from ligand atomic orbitals, and of another set of bands (their filling depends on the electron count at metal) at a smaller binding energy originating only from the metal atomic orbitals. A more realistic picture of bonding assumes a small admixture of ligand states to the ‘metal band’ and a small admixture of metal states to the bottom ‘ligand band’. As the oxidizing character of a metal cation and/or the reducing character of the ligand anion increase, the DOS maxima become less separated in the energy scale, and the mutual mixing of M and L orbitals is more efficient. At one extreme case, an inversion of the metal and ligand states may take place (i.e. when metal d orbitals contribute more partial DOS to the ‘L’ band than to the initial ‘M’ band).

It turns out that the entire series of such simplified mixing scenarios is nicely exemplified in the X-ray photoelectron spectra of the fluorides of Ag(I), Ag(II) and Ag(III) [18]. Here, X-ray photoelectron spectra trace back mostly the partial contribution from the $4d$ orbitals of Ag to the total DOS (due to a much larger cross section for interaction of the Ag($4d$) rather than F($2p$) electrons with X-ray radiation). AgF is a classic case of a quasi-ionic compound; the contribution from the $4d$ orbitals to the ‘metal band’ is *ca* nine times larger than that to the ‘ligand band’. Covalence substantially increases for AgF₂; many $4d$ states are found in the band placed at higher binding energy and the corresponding ratio is now close to 2:1. Finally, one can observe an inversion of the roles of ‘metal’ and ‘ligand’ for KAgF₄, a Ag(III) compound, with 60% of the $4d$ states sitting in the ‘ligand band’ (!).³ These experimental results agree very well with the

³Regretably, binary AgF₃ could not have been studied in this series due to its inherent instability in high-vacuum conditions.

results of the quantum mechanical density functional theory (DFT) calculations for these systems [11,18]. To the best of our knowledge, KAgF_4 is the first experimentally documented case of ‘inversion’ of the valence states in a neutral complex in which the ligand is a genuine non-metal (one should note that ‘inverse crystal field’ systems have been theorized by some in the past [19–21]).⁴ Similar phenomenon is supposed to take place for other strong oxidizers, such as PtF_6 , and for the metastable systems at the verge of the hindered internal redox reaction.

The highly oxidizing nature of Ag(II) and Ag(III) , which is linked primarily to valence electrons, also influences the core states of the neighbouring ligands. For example, the binding energy of the F(1s) electrons for the above-mentioned KAgF_4 is 686.25 eV, which is by nearly 3 eV larger than the corresponding value for AgF [18], and supposedly the largest value ever measured in a fluorine compound. It is important to realize that fluorine is considered to be *the most electronegative* of chemical elements, and the one which forms predominantly ionic bonds to all metallic elements. A recent study has shown that the core states of Ag may be affected as well; thus, the binding energy of $\text{Ag}(3d_{5/2})$ states reaches as much as 370.1 eV for AgSO_4 , a Ag(II) compound [23]; this is again the largest value found in the literature and by over 2 eV more than the corresponding value for Ag_2SO_4 , i.e. a ‘common’ silver(I) sulfate. To put it in another way—the reactive hole in the valence $4d$ shell of silver gets easily shared with the valence and core states of neighbouring elements and it also gets transferred to the core states of Ag.

4. Free (and) radical: a contagious disease

Since Ag(II) cation is a spin-1/2 species, it exhibits a free radical character just like the isoelectronic Cu(II) or Ni(II) siblings. Thus, the (substantial) hole transfer from Ag(II) to the chemically bound atoms in its first coordination sphere (discussed in the previous section) is in fact equivalent to the (substantial) decrease of the free radical character at Ag(II) and its concomitant increase at the ligands. In other terms: Ag(II) serves as a powerful ‘spin polarizer’ towards the surrounding matter. The transfer of spin may be appreciable, as indicated by the quantum mechanical DFT calculations for a number of solid-state systems. For example, the calculated magnetic moment on Ag(II) cation in ferromagnetic Cs_2AgF_4 slightly exceeds $0.5 \mu_B$ while the corresponding value for each F anion is $0.1 \mu_B$ [24]. This means that the unpaired electron density at four F ligands surrounding silver is $0.4 \mu_B$, *comparable* with that at the central Ag(II) cation. Another remarkable example is that of antiferromagnetic AgSO_4 [25]; here Ag(II) preserves the absolute magnetic moment of only *ca* $0.42 \mu_B$ while the absolute magnetic moment on O atoms reaches up to $0.09 \mu_B$ (recall: these ‘oxide anions’ are not free but they are covalently bound to sulfur atom!). The corresponding values for Cu(II) sulfate are: $0.80 \mu_B$ (Cu) and up to $0.03 \mu_B$ (O) [25]. Strong spin polarization is seen even in such systems where the non-metal cannot attain large magnetic moment due to symmetry constraints. KAgF_3 perovskite is one good example. Here, the shortest Ag–F–Ag links of the antiferromagnetically ordered infinite $(\text{AgF})^+$ chains are much closer to linear (154°) than to a right angle (90°) [26]; magnetic moment on F atom would be null for the 180° case, and thus it deviates only slightly from zero for KAgF_3 . Nevertheless, spin polarization at F (i.e. excess of alpha spin at one side and its deficiency at the other side of the atom) is clearly visible in the projection of magnetic density (figure 4).

We will now discuss two important manifestations of large spin density present at ligands bound to Ag(II) in its compounds.

5. Bonus: easy spin exchange

The presence of free spin at Ag(II) centres implies a possibility of magnetic ordering of Ag(II) -rich compounds in the solid state, as is well researched for related Cu(II) systems. The great majority of (even ‘magnetically dense’ i.e. Ag(II) -rich) compounds form lattices with rather isolated Ag(II)

⁴Very little has been published on ‘inverse crystal field’. Our knowledge comes mostly from the copy of the talk given by Roald Hoffmann (see [22] and references therein).

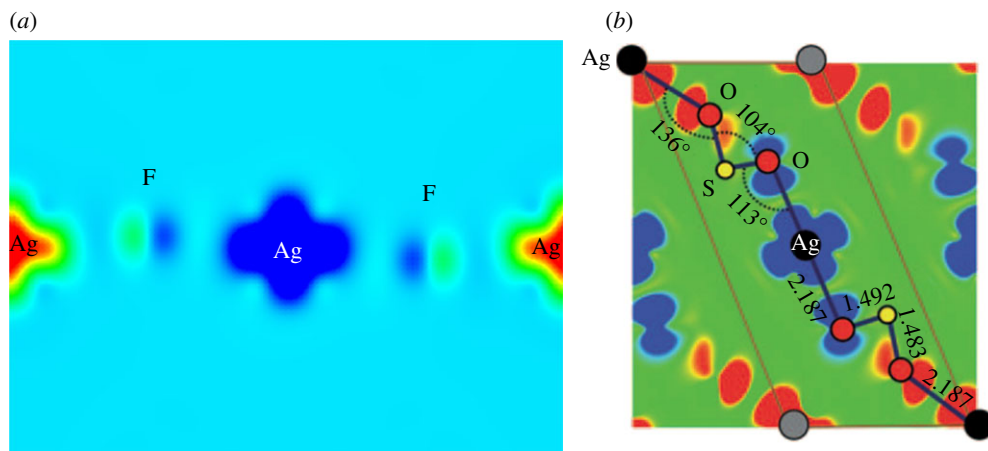


Figure 4. (a) Projection of the calculated spin density along the $(\text{AgF})^+$ infinite chain in KAgF_3 perovskite [26]. Red and dark blue colours denote maxima of alpha and beta density, respectively. Note the marked polarization of the bridging F atoms. (b) Projection of the calculated spin density along the $[\text{Ag}(\text{SO}_4)]$ infinite chain in AgSO_4 [25]. Red and dark blue colours denote maxima of alpha and beta density, respectively. Note the marked polarization of the OO bridge and spin density omitting S atoms.

centres; these systems are paramagnetic and they usually order magnetically at low or moderate temperatures. $\text{Ag}(\text{SbF}_6)_2$ is one good example, with its paramagnetic Curie temperature (θ) of +3 K, as derived from the fit of magnetic susceptibility versus temperature dependence to the Curie–Weiss law [27]. Here, there is little benefit from large spin density being present at both cation and surrounding anions since the superexchange pathway between $\text{Ag}(\text{II})$ centres is long, complex, kinked, and it consists partly of quite ionic bonds. The true potential of $\text{Ag}(\text{II})$ salts in terms of their magnetic properties is best revealed in systems where a network of uninterrupted short covalent links exists in at least one (or more) dimensions in the crystal lattice (preferably when a single non-metallic atom constitutes the bridge). In such systems, there is a substantial spin on *both* metal centre and ligand which leads to very large magnetic superexchange constants, and the propagation of strong magnetic interactions is facile in the direction(s) of network propagation.

For example, antiferromagnetic AgSO_4 exhibits a strong quasi-one-dimensional superexchange along the infinite $[\text{Ag}(\text{SO}_4)]$ chains characterized by a superexchange constant, J , of -18.7 meV [25].^{5,6} This number is impressive while taking into account that the superexchange pathway formally consists of three atoms, i.e. of the OSO bridge. Note that similar J value (-19 meV) is observed for antiferromagnetic NiO , with the monoatomic bridge (O atom) between the Ni centres, and as many as two unpaired electrons per site ($\text{Ni}(\text{II})$ in high-spin d^8 configuration). Closer inspection of the calculated spin density in AgSO_4 shows that the superexchange pathway in fact omits the sulfur atom as it polarizes the $\text{O} \cdots \text{O}$ bridge. This is peculiar, since no chemical bond exists between the neighbouring O atoms of the sulfate anion. Clearly, $\text{Ag}(\text{II})$ cation is capable of spin-polarizing the adjacent anion so strongly that it induces a fractional chemical bonding between O atoms. We will come back to this unusual feature in §8.

KAgF_3 is another exemplification of very strong magnetic superexchange in $\text{Ag}(\text{II})$ systems. Although its crystal structure is related to that of the KZnF_3 perovskite, the small local distortions of the AgF bond lengths and the Ag-F-Ag bond angles lead to a quasi-one-dimensional structure

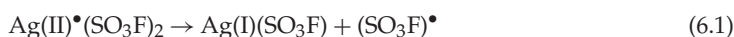
⁵The J constant given in the original paper must be multiplied by 2 to comply with the magnetic Hamiltonian used in other works. A slightly smaller absolute value ($J = -15.4 \text{ meV}$) has been measured for $\text{Ag}_3(\text{SO}_3\text{F})_4$ with its infinite $[\text{Ag}(\text{SO}_3\text{F})^+]$ chains [28].

⁶For more precise description of the crystal structure of AgSO_4 , the reader is referred to [29].

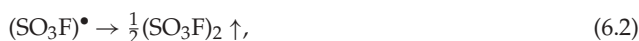
with the antiferromagnetically ordered infinite $(\text{AgF})^+$ chains present in the crystal structure (figure 4) [26]. Here, the bridge between Ag(II) centres is monoatomic, and it is not far from linear; hence a strong superexchange is anticipated. Indeed, it turns out that the J values exhibited by the high- and low-temperature phases of this compound are close to, respectively, -100 meV and -120 meV [30]. These are giant J values, indeed. The quantum mechanical calculations show that J values of about -180 meV are expected for Rb and Cs analogues of KAgF_3 , with their linear $(\text{AgF})^+$ chains [31]. Recall that the absolute values of J exceeding 150 meV are typical of *only one family* of compounds, the oxocuprates(II), which are isoelectronic to fluoroargentates(II). For example, the J values measured for La_2CuO_4 (two-dimensional system) and Sr_2CuO_3 (one-dimensional system) equal -146 meV [32] and -254 meV [33], respectively. Actually, the latter absolute value is *record large* in solid-state physics, but our calculations show that *even larger* absolute values approaching 300 meV are possible for some Ag(II) systems [24]. The quest for such unusual magnetic materials now continues in our collaborating laboratories.

6. Price to pay: low thermal stability

Aside from the benefits taken from the (partly) free radical character of Ag(II) and of the neighbouring ligands, there is also a price to pay. The price is a low thermal stability of most compounds containing Ag(II) cations. This is connected with a possibility of the full transfer of the spin density from Ag(II) to a ligand, for example:

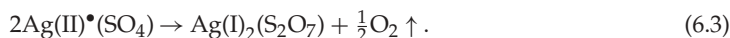


and



where the superscript dot stands for a 'free radical' [34]. The free radicals $(\text{SO}_3\text{F})^\bullet$ eliminated in the process (equation (6.1)) get coupled into a volatile peroxide (equation (6.2)). The reaction is not only entropically driven, but it is also exothermic, which points to the lack of thermodynamic stability of the Ag(II) precursor. Indeed, all compounds of Ag(II) with O, N, C or S ligands share the same fate (see [12] and references therein). The majority of F connections of Ag(II) are thermodynamically stable; elimination of F_2 becomes facile only for Ag(III) derivatives, such as AgF_3 (at temperatures above 20°C) or AgF_4^- salts (at temperatures above $+300^\circ\text{C}$ and in dynamic vacuum [30]).

Lack of thermodynamic stability of certain Ag(II) salts may be rather pronounced as exemplified by AgSO_4 . This black compound decomposes thermally at temperatures above 110°C according to the following equation:



Nevertheless, Ag(II)SO_4 is metastable at ambient (p,T) conditions and despite the fact that the equilibrium pressure of oxygen exceeds 1TPa (*sic!*). However, AgSO_4 undergoes slow decomposition yielding the low-pressure form of $\text{Ag(I)}_2(\text{S}_2\text{O}_7)$ at ultra-high vacuum conditions [23] and yielding the high-pressure form of $\text{Ag(I)}_2(\text{S}_2\text{O}_7)$ at pressures exceeding 23GPa in a diamond anvil cell [29].

7. Distortions: small but stubborn

As for all 'localized' d^9 systems, the compounds in the solid state containing Ag(II) are susceptible to a Jahn–Teller (JT) effect. The JT effect for related Cu(II) compounds induces rather small distortions of the first coordination sphere, and the cases are known where the difference between the equatorial and apical Cu–ligand bond lengths does not exceed 2%. However, the JT effect for Ag(II) compounds is quite strong as it usually leads to appreciable elongation (or, rarely, shortening) of the $[\text{AgL}_6]$ octahedron [11]. Indeed, the square-planar coordination of Ag(II) cation is frequently encountered in these systems. Even for elongated octahedral coordination the

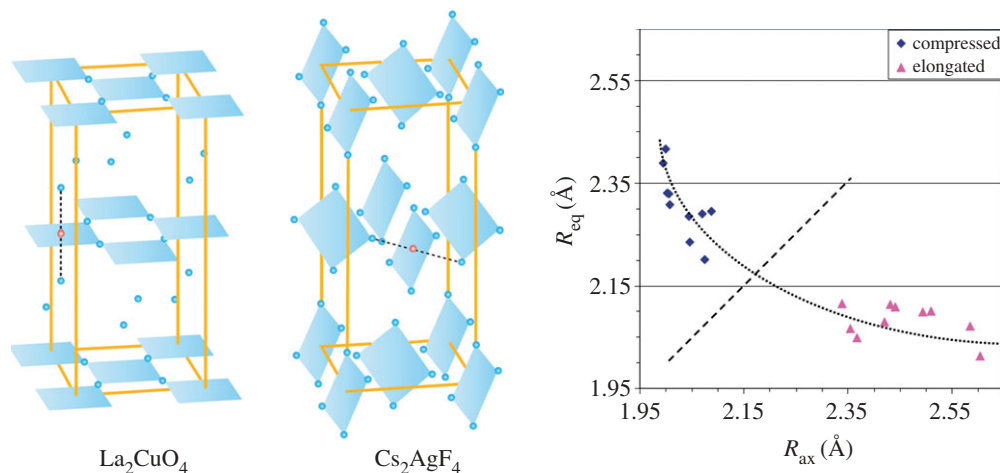


Figure 5. (a) Comparison of the crystal structures of isoelectronic and quasi-isostructural La_2CuO_4 and Cs_2AgF_4 . The arrangement of the $[\text{ML}_4]$ square-planar units is shown (blue squares) together with the two long apical ML distances (dotted lines). (b) Illustration of the plasticity of the $[\text{AgF}_6]$ coordination sphere for *ca* 20 Ag(II) fluoride systems. R_{eq} and R_{ax} stand for equatorial and axial bond lengths, respectively.

difference between the apical and equatorial Ag–ligand bond lengths in Ag(II) fluorides usually exceeds 5% (for compressed octahedron) or even 10% (for elongated octahedron) [35] (figure 5). This has to do with the differences between the $3d$ and $4d$ transition metals and in particular with the increased spatial extent of the $d(z^2)$ lone pair of the divalent cations as one goes down Group 11 of the Periodic Table. The plasticity of the first coordination sphere of Ag(II) (due to *one* unpaired electron) is quite large [28], larger than flexibility measured for compounds of Cu(II) [36], and it resembles the behaviour of principal + secondary interactions (due to *two* paired electrons) typical of hypervalent compounds [37].

There are at least three important practical reasons for interest in the strength of the JT effect and associated structural distortions in compounds of Ag(II) aside from scientific curiosity. First, the JT effect is always related to a certain energetic stabilization. It has been argued that this stabilization may be small when compared with other contributions to enthalpy at high pressures, and in consequence the JT effect may disappear [38]. For certain Cu(II) compounds, this effect has been predicted to take place at *ca* 30 GPa, but no estimates are available for Ag(II) systems.⁷ Second, these are small collective distortions of the crystal lattice (collective JT effect) which have huge impact on magnetic properties. For example, Cs_2AgF_4 is close-to-isostructural to La_2CuO_4 [39] yet these are small lattice distortions of the latter which lead to the ferromagnetic rather than antiferromagnetic ground state of Cs_2AgF_4 [40] (figure 5). Third, the elimination of the JT effect at high pressure is likely to lead to a metallization of a Ag(II) compound (cf. §9).

The robustness of the JT effect has been experimentally and theoretically tested for Ag(II)SO_4 [29]. It turns out that the initially large JT distortion revealed in quite different Ag–O bond lengths (2.14 versus 3.04 Å, or a 42% difference) decreases at a moderate pressure of 30 GPa (2.03 versus 2.40 Å, or an 18% difference). This result may be viewed as impressive but at the 18% bond length difference the JT effect is still far from disappearing.

⁷In principle, packing of balls of different sizes (i.e. disproportionation to Ag(I) and Ag(III)) or of ellipsoids (Ag(II) cation being unspherical due to the JT effect) may be more efficient than that of ideal spheres. It is thus likely that ideal octahedra would not achieve better packing coefficient than the distorted ones.

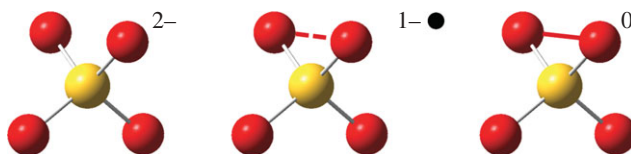


Figure 6. Illustration of the $\text{Ag(II)}^\bullet(\text{SO}_4^{2-}) \leftrightarrow \text{Ag(I)}(\text{SO}_4^{1-\bullet}) \leftrightarrow \text{Ag(0)}(\text{SO}_4^0)$ tautomerism as discussed in the text. Dashed and solid red lines stand for a partial (bond order 1/2) and a single chemical bond between two O atoms of the $[\text{SO}_4]$ unit.

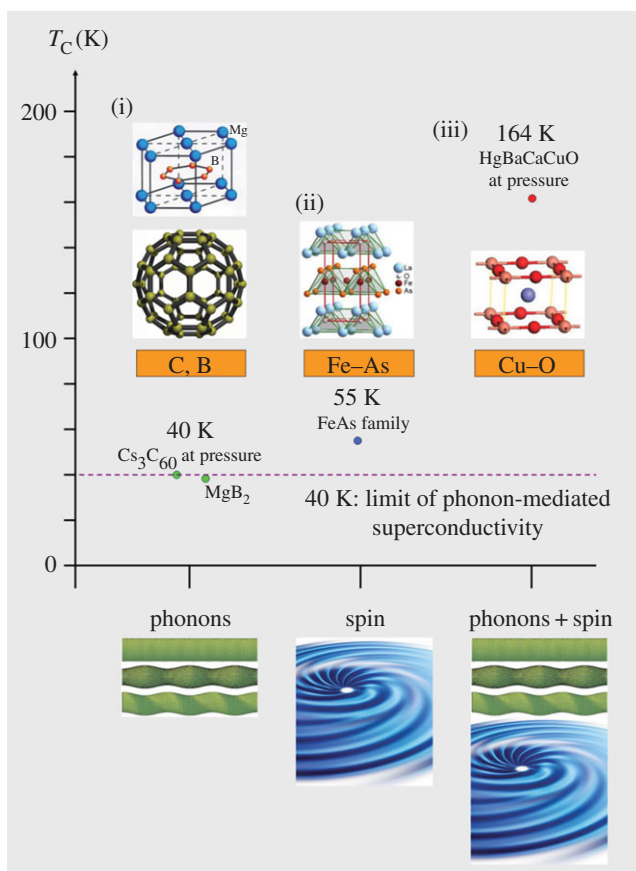
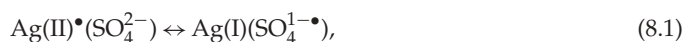


Figure 7. Illustration of the three vital mechanisms of enhancement of the superconducting critical temperature, T_c , in diverse families of superconductors: (i) the classical phonon (i.e. phonon–electron coupling) mechanism, with the current T_c record of *ca* 40 K, (ii) the magnetic fluctuations mechanism (particularly for doped layered antiferromagnetic systems), with the current T_c record of *ca* 55 K, and (iii) the synergic phonon and magnetic mechanism (plus other contributions), operative for doped oxocuprates(II), the current record holders of the T_c value. Doped fluoroargentates(II), which are isoelectronic to oxocuprates and exhibit strong low-dimensional magnetic interactions in the undoped state would probably fall in category (iii).

8. Electromers: Dr Jekyll and Mr Hyde

We have seen that in the previously discussed case of AgSO_4 (§4) the spin density is spread substantially over ligands, while Ag(II) preserves the magnetic moment of only $0.42 \mu_B$ as contrasted with the expected value of *ca* $1.0 \mu_B$. This may be illustrated with the following simplified equation:



where the 50–50% shares of free spin on metal and ligand are assumed. In this case, a partial bond (with bond order of 1/2) exists between two O atoms of the $[\text{SO}_4]$ unit (figure 6). An even more extreme division of the electronic density in the $[\text{SO}_4]$ unit might be that of $\text{Ag}(0)(\text{SO}_4^0)$ where now the single bond formally exists between two O atoms of the (SO_4^0) peroxide (figure 6). While the latter Lewis formula is certainly far from being realistic, the former one is not. Significant departure of the nature of AgSO_4 from the ‘ionic model’, existence of the substantial spin polarization at O atoms (figure 4), with the OO bridge resembling a partial bond, as well as facile transfer of holes to the $\text{O}(2p)$ band (implied by the evolution of O_2 upon heating, §6) suggest that it could be possible to prepare an electronic isomer (*electromer*) of AgSO_4 in the form of $\text{Ag}(\text{I})(\text{SO}_4^{1-\bullet})$, i.e. an equivalent of $\text{Ag}(\text{I})_2(\text{S}_2\text{O}_8)$, a hypothetical silver(I) peroxodisulfate. The tautomeric relationship between these two distinct forms of one compound (‘Dr Jekyll and Mr Hyde’) could be illustrated as follows:



White $\text{Ag}(\text{I})_2(\text{S}_2\text{O}_8)$, a cousin of the well-known alkali metal peroxodisulfates, and electromeric sibling of black $\text{Ag}(\text{II})\text{SO}_4$, has indeed been prepared very recently in our laboratories and it will be reported shortly in a separate contribution.

9. Conclusion and outlook

Here we have succinctly described selected chemical and physical properties of the compounds of divalent silver. We have pointed out a large number of peculiar features of these systems, which render them interesting for various applications. High reactivity and strong oxidizing properties make them attractive as reagents for demanding and exhaustive redox reactions in organic and inorganic chemistry. The capability of introducing large share of spin on neighbouring ligands makes them attractive for use as magnetic materials, and in spintronics [41]. Electronic tautomerism (*electromerism*) has been anticipated for $\text{AgSO}_4/\text{Ag}_2\text{S}_2\text{O}_8$; it is interesting whether this kind of isomerism, typical rather for inorganic–organic hybrid systems, could be of any practical use, for example, in data storage (0–1 switching). Probably most interesting is the possibility of generating of high- T_C superconductivity in doped $\text{Ag}(\text{II})$ systems [11,42].⁸ Doped fluoroargentates(II), which are isoelectronic to doped oxocuprates(II) and exhibit very strong low-dimensional magnetic interactions in the undoped state, would probably benefit from the synergistic mechanism of T_C enhancement, typical of doped oxocuprates(II) (figure 7). Last but not the least, an intriguing possibility appears of nivelating of the JT effect in the compounds of $\text{Ag}(\text{II})$ at elevated pressure. These and other interesting phenomena and compounds are currently explored.

Data accessibility. No restrictions apply on the availability of research materials or data.

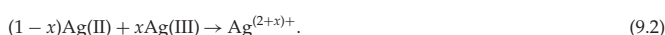
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⁸This goal requires that a successful doping may be realized to two-dimensional $[\text{AgL}_N]$ lattices and that the dopant will not localize as a defect of crystal lattice, but rather it will compropionate with the $[\text{AgL}_N]$ matrix, for example:



and



The currently known rare examples of mixed valence compounds of silver are disproportionated. The quest continues for a two-dimensional system with equally strong antiferromagnetic interaction, which could serve as a precursor towards a room-temperature superconductor.

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