

# Ligation of Aza bases to the $\text{AgF}_2$ molecule: a theoretical study

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**Abstract** We have analyzed the electronic structure and chemical bonding for molecular adducts of the  $\text{Ag(II)F}_2$  molecule with various aza Lewis bases including ammonia, nitriles, secondary amines, and their derivatives exhibiting various degrees of fluorination. Density functional theory calculations indicate that a progressive shift occurs of the spin density from the Ag center towards the coordinating nitrogen atoms of aza ligands, as the ligation energy increases. Chemistry of  $\text{Ag(II)}$  might be extended with little effort beyond the known aza connections, to include nitriles, perfluorinated nitriles and perfluorinated amines.

**Keywords** Fluorides · Aza ligands · Silver · Density functional theory

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This work is dedicated to memory of Wojciech Ochmański, unforgettable person, good-hearted man, whose craftsmanship in work was second-to-none.

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## Introduction

Divalent silver ( $\text{Ag}^{\text{II}}$ ) is the most potent *one*-electron oxidizer among all chemically attainable  $\text{M}^{2+}$  cations [1–3], capable of oxidizing of the  $\text{O}^{2-}$  and  $\text{Cl}^-$  anions [4]. In consequence, chemistry of divalent silver has been traditionally predominated by anionic fluoride derivatives, such as  $\text{F}^-$ ,  $\text{BF}_4^-$ ,  $\text{SbF}_6^-$ , etc. [1–3]. However, ligation of strong Lewis bases to metal cations usually allows for significant reduction of the standard redox potential, thus stabilizing high oxidation states of the chemical elements. Therefore, over two dozens compounds of  $\text{Ag}^{\text{II}}$  with aza bases, such as for example pyridine, have been synthesized in the past using wet chemistry (peroxodisulphate) route [5–8]. In majority of these complexes  $\text{Ag}^{\text{II}}$  is coordinated by *four* aza ligands, L, and by two charge-compensating anions, X, thus forming molecular  $\text{AgL}_4\text{X}_2$  crystals. In addition, quite unusual  $\text{Ag}^{\text{II}}\text{-C}$  and  $\text{Ag}^{\text{II}}\text{-N}$  bonds exist in a few porphyrine derivatives [9, 10]. Also these complexes show molecular nature *par excellence*. Obviously, magnetic coupling between  $\text{Ag}^{\text{II}}$  centers is inherently weak in all these magnetically-dilute 0D compounds and their magnetic ordering temperatures do not exceed several degrees Kelvin.

Further extension of the coordination chemistry of  $\text{Ag}^{\text{II}}$  would be valuable for a generation of a 2D structure which contains flat  $[\text{AgF}_2]$  sheets at the elongated octahedral coordination of  $\text{Ag}^{\text{II}}$  at a noticeable magnetic coupling between  $\text{Ag}^{\text{II}}$  centers [11]. Such structural leitmotif-previously theorized to induce high-temperature superconductivity in fluoroargentates [1–3, 12–14] has not yet been obtained in experiment [15–17]. With this in mind, we have theoretically analyzed bonding in fourteen distinct trans- $\text{AgL}_2\text{F}_2$  molecules containing *two* aza bases, L, ligated to the  $\text{Ag}^{\text{II}}$  center. As far as we know, theoretical and experimental studies have not yet been performed for the systems in

question. The  $\text{AgL}_2\text{F}_2$  stoichiometry (as contrasted with the well known  $\text{AgL}_4\text{X}_2$  solids described above) is important because these molecules might constitute gas-phase precursors of the magnetically-ordered 2D solids, which contain  $[\text{AgF}_2]$  layers with axially coordinated ligands L [11]. Another important reason for studying the entire family of the  $\text{AgL}_2\text{F}_2$  molecules with chemical properties of L varying across the series, is to indicate these organic ligands, which are capable of stabilizing  $\text{Ag}^{\text{II}}$  without being themselves oxidized [18–20].

## Methods

We have applied the unrestricted density functional theory (DFT) method with the B3LYP correlation-exchange functional, the 6-311++G\*\* Pople basis set for H, C, N, F, Cl and the relativistic LANL pseudopotentials for Ag followed by double dzeta basis for valence electrons. The unrestricted B3LYP method has been previously applied to the  $\text{AgF}_2$  molecule and yielded results similar to ones obtained with the more time-consuming MP2 and CCSD(T) methods [21]. Calculation of the harmonic vibrations for all molecules under study yielded no imaginary modes. The optimized geometries of all molecules are given in the *ESM*. In Table 1 we collect numerical data, including the Ag-F and Ag-N bond lengths, and the Mulliken spin densities on Ag and on the neighbouring F and N atoms. Zero Point Energy (ZPE) correction has been used for calculations of the ligation energy.

**Table 1** The Ag-F and Ag-N bond lengths,  $R(\text{Ag-F})$  and  $R(\text{Ag-N})$  / Å, spin density on Ag and on the neighbouring F and N atoms,  $\rho(\text{Ag})$ ,  $\rho(\text{F})$  and  $\rho(\text{N})$  /e, respectively, molecular symmetry and ligation

Ligand	$R(\text{Ag-F})$ /Å	$R(\text{Ag-N})$ /Å	$\rho(\text{Ag})$ /e	$\rho(\text{F})$ /e	$\rho(\text{N})$ /e	Symmetry	$\Delta E_L$ /eV <sub>L</sub>
–	1.980	–	0.569	0.215	–	$D_{\infty h}$	0.00
$\text{NF}_3$	2.003	2.574	0.488	0.199	0.048	$C_{2h}$	–0.60
NC-CN	2.037	2.344	0.488	0.213	0.074	$D_{2h}$	–0.78
NC-CF <sub>3</sub>	2.039	2.338	0.483	0.213	0.071	$C_2$ ( $\sim C_{2h}$ )	–0.82
NC-F	2.045	2.313	0.470	0.213	0.057	$D_{2h}$	–0.96
NC-CCl <sub>3</sub>	2.046	2.310	0.472	0.212	0.076	$C_1$ ( $\sim C_2$ )	–0.96
NC-H	2.051	2.299	0.466	0.213	0.074	$D_{2h}$	–1.02
$\text{N}_2\text{C}_4\text{F}_4$	2.042	2.347	0.448	0.200	0.076	$D_{2h}$	–1.05
$\text{N}_2\text{C}_4\text{H}_2\text{F}_2^{\text{F}*}$	2.050	2.325	0.438	0.199	0.078	$D_{2h}$	–1.24
$\text{NF}_2\text{H}^{**}$	2.063	2.357	0.393	0.180	0.099	$C_{2h}$	–1.24
NC-CH <sub>3</sub>	2.062	2.262	0.460	0.211	0.083	$C_2$ ( $\sim C_{2h}$ )	–1.27
$\text{NH}_2\text{F}^{**}$	2.078	2.281	0.386	0.185	0.114	$C_{2h}$	–1.74
$\text{NH}_3^{**}$	2.092	2.241	0.400	0.183	0.130	$C_{2h}$	–2.16
$\text{N}_2\text{C}_4\text{H}_2\text{F}_2^{\text{H}*}$	2.084	2.218	0.413	0.175	0.116	$D_2$	–2.17
$\text{N}_2\text{C}_4\text{H}_4$	2.095	2.209	0.405	0.170	0.121	$D_2$	–2.41

\* Superscript indicates, which atoms of 2,2'-difluoro-1,4-diazabenzene, are closer to  $\text{Ag}^{\text{II}}$ .

\*\* Species containing the F...H hydrogen bonds.

Respective values for non-complexed binary  $\text{AgF}_2$  are shown for comparison. Entries are shown in the order of the decreasing value of  $\Delta E_L$ .

## Results

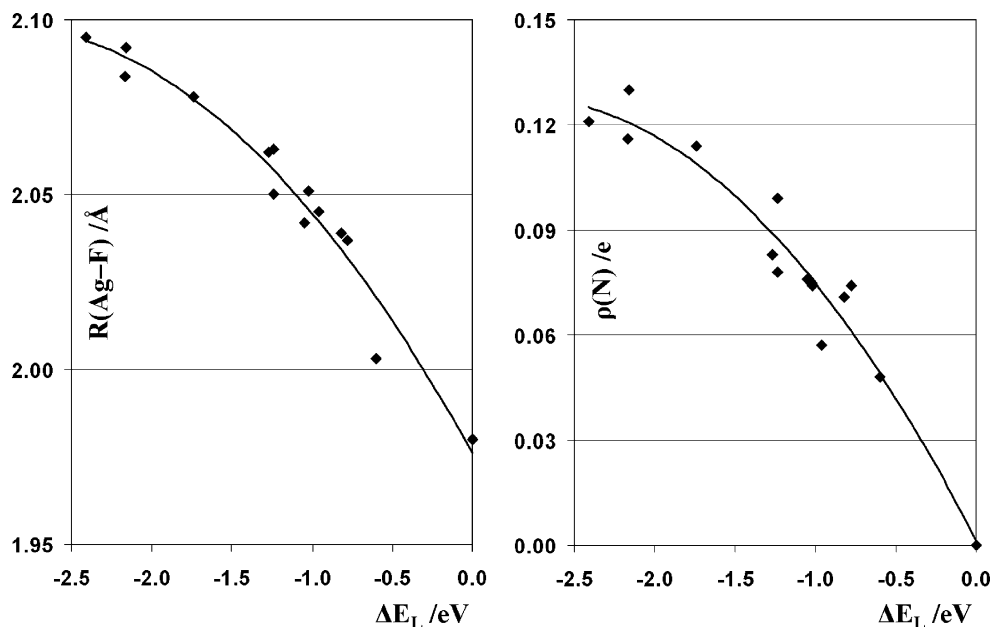
The  $\text{Ag}^{\text{II}}$  center in the  $\text{AgF}_2$  molecule is coordinatively unsaturated (CN=2), the typical CN of  $\text{Ag}^{\text{II}}$  being equal to 6 (4+2 or 2+4) [1–3, 22].  $\text{Ag}^{\text{II}}$  can therefore easily bind at least two (and even up to four) additional ligands, such as the aza species studied here. The values of the ligation energy,  $\Delta E_L$  (i.e. the ZPE-corrected energy of the reaction:  $\text{AgF}_2 + 2 \text{L} \rightarrow \text{F}_2\text{AgL}_2$ ) densely fill a broad range from –0.6 eV for  $\text{NF}_3$  (a very poor  $\sigma$  donor) to –2.4 eV for pyrazine (an excellent  $\sigma$  donor), at the corresponding values of the  $\text{Ag}^{\text{II}}\text{-N}$  bond lengths ( $R(\text{Ag-N})$ ) varying from 2.574 Å to 2.209 Å. Not surprisingly, a nice monotonic relationship exists between  $\Delta E_L$  and  $R(\text{Ag-N})$  (Fig. 1).

Fluorination of the aza ligand significantly decreases the strength of the acid/base interaction between  $\text{AgF}_2$  and the aza compound, as noted for four series of ligands independently: (i)  $\text{NH}_3 > \text{NH}_2\text{F} > \text{NHF}_2 > \text{NF}_3$ , (ii)  $\text{NCH} > \text{NCF}$ , (iii)  $\text{NC-CH}_3 > \text{NC-CF}_3$ , and (iv)  $\text{N}_2\text{C}_4\text{H}_4 > \text{N}_2\text{C}_4\text{H}_2\text{F}_2^{\text{H}} > \text{H}_2\text{C}_4\text{H}_2\text{F}_2^{\text{F}} > \text{N}_2\text{C}_4\text{F}_4$ . The *perfluorination* leads to the decrease of the absolute value of the energy of ligation by 6% (NCF), 35% (NCCF<sub>3</sub>), 56% (N<sub>2</sub>C<sub>4</sub>F<sub>4</sub>) and even up to 72% (NF<sub>3</sub>), as compared to their non fluorinated analogues. This is obviously due to the strong inductive effect of the electron-withdrawing F substituent.

As the strength of ligation of  $\text{Ag}^{\text{II}}$  by aza base increases, the N atom adjacent to the  $\text{Ag}^{\text{II}}$  center shares more and more of the unpaired electron (spin) density (Table 1). Indeed, another monotonic relationship exists between the value of  $\Delta E_L$  and the Mulliken spin density on the N atom,

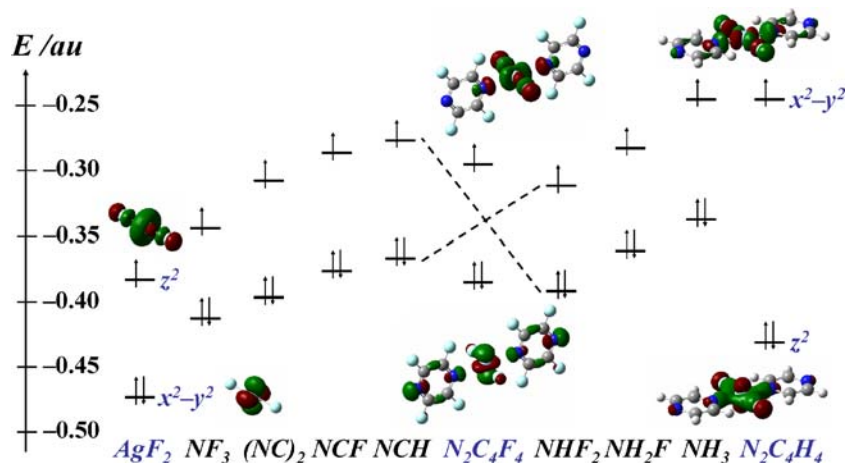
energy,  $\Delta E_L$  /eV (see text), for fourteen *trans*- $\text{F}_2\text{AgL}_2$  molecules containing divalent silver and monodentate aza ligands (L)

**Fig. 1** The monotonic relationships between the value of the ligation energy,  $\Delta E_L$ , and the  $\text{Ag}^{\text{II}}$ -N bond length,  $R(\text{Ag-N})$  (left), and between  $\Delta E_L$  and the Mulliken spin density on the N atom,  $\rho(\text{N})$  (right)



$\rho(\text{N})$  (Fig. 1). The progressive shift of spin density from  $\text{Ag}^{\text{II}}$  towards the ligand makes the aza derivatives similar to the recently studied oxo derivatives of  $\text{Ag}^{\text{II}}$  [17]. It seems that increased basicity of a ligand (its willingness to share MO corresponding to an electron pair) is correlated with the redox behaviour of a ligand (its willingness to introduce a hole into the same orbital). One important difference between aza and oxo ligands is, however, that the values of  $\rho(\text{N})$  (ranging from 0.05 e to 0.13 e) are noticeably smaller than the typical values of  $\rho(\text{O})$  (ranging from 0.16 e to 0.43 e for singly charged ionic ligands ( $\text{SO}_3\text{F}^-$ ,  $\text{ClO}_4^-$ , etc) [17]). This is mostly due to electroneutral character of

aza ligands as compared to their negatively charged oxo counterparts. Since the absolute spin density on the ligand may be qualitatively correlated with the thermal stability of the compound [17], we think that most of the aza complexes studied here should *not* undergo the undesirable auto-redox reactions (which involve the reduction of  $\text{Ag}^{\text{II}}$ ). Therefore, it seems that chemistry of  $\text{Ag}^{\text{II}}$  might be successfully extended beyond the known aza connections [9, 10], to include also nitriles, perfluorinated nitriles and perfluorinated amines. It would be interesting to approach synthesis of selected complexes listed in Table 1, either as isolated molecules or in the solid state.



**Fig. 2** Energy ( $E$ /atomic units) of the  $d(z^2)$  and  $d(x^2-y^2)$   $\alpha$  orbitals for the  $\text{AgF}_2$  molecule and for its nine complexes with selected aza ligands, arranged in the order of the increasing ligation strength (from left to right). The higher-energy orbital usually corresponds to SOMO;

for numerical values of  $E$  see [ESM](#). Orbitals were illustrated for  $\text{AgF}_2$  and for its adducts with  $\text{N}_2\text{C}_4\text{F}_4$  and  $\text{N}_2\text{C}_4\text{H}_4$ . Note the ‘crossing’ of the  $d(z^2)$  and  $d(x^2-y^2)$  levels which occurs at the intermediate ligation strength, for  $[\text{AgF}_2(\text{N}_2\text{C}_4\text{F}_4)_2]$

Most of spin density resides on the  $d(z^2)$  orbital of Ag for the isolated  $\text{AgF}_2$  molecule, the  $d(x^2-y^2)$  orbital serving mostly as a ‘lone pair’ (Fig. 2). This is also the case for the adducts of  $\text{AgF}_2$  with weakly coordinating aza ligands, such as  $\text{NF}_3$  or  $\text{NCH}$ . However, the picture of electronic structure changes dramatically as the ligation strength of the aza base increases. This is exemplified by adducts of  $\text{AgF}_2$  with ammonia and with pyrazine, where  $\text{SOMO}(\alpha)$  corresponds mostly to the  $d(x^2-y^2)$  orbital, the  $d(z^2)$  function taking up the role of a ‘lone pair’. The case when aza ligand is more strongly bound to  $\text{Ag}^{\text{II}}$  than fluoride anions is obviously not favourable for generation of the extended 2D structure containing the  $[\text{AgF}_2]$  sheets, with the elongated octahedral coordination of Ag. The most complex electronic structure corresponds to an intermediate situation, when the (formally electroneutral) aza ligand becomes equally strongly bound to  $\text{Ag}^{\text{II}}$  as is the (formally negatively charged) fluoride anion. Such ‘orbital crossing’ is seen for example for the  $[\text{AgF}_2(\text{N}_2\text{C}_4\text{F}_4)_2]$  composition (see Fig. 2); it is difficult to distinguish between the  $d(x^2-y^2)$  and  $d(z^2)$  functions, which mutually mix with each other in an appropriate ligand environment.

## Summary

In conclusion, our DFT calculations indicate that:

- (i) the ligation energy,  $\Delta E_L$ , and the Mulliken spin density on the N atom,  $\rho(\text{N})$ , are monotonically correlated;
- (ii) aza bases exhibit much smaller values of the Mulliken spin density than majority of anionic oxo ligands [17], which explains marked stability of the aza complexes of  $\text{Ag}^{\text{II}}$ ;
- (iii) fluorination of the aza ligand significantly decreases the free spin residing on the organic ligand, thus making it less susceptible to oxidation by  $\text{Ag}^{\text{II}}$ ; unfortunately, the strength of the acid/base interaction between  $\text{AgF}_2$  and the aza species simultaneously decreases, which may preclude formation of the  $\text{AgL}_2\text{F}_2$  complexes.

Further theoretical and experimental investigations of the fascinating  $\text{Ag}^{\text{II}}$  adducts with aza bases, are currently underway in our laboratory.

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