crystals

SUPLEMENTARY INFORMATION

Quest for Compounds at the Verge of Charge Transfer Instabilities: the Case of Silver(II) Chloride

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This work is dedicated to the memory of Kazimierz Fajans (1887–1975)

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S1 Analysis of halogen-halogen interactions

All predicted polymorphs contain very short non-bonding Cl…Cl distances that are being considerably shorter than sum of chlorine van der Waals radii (3.62 Å). Our analysis points to presence of type-I and type-II Cl…Cl bonding in the predicted $AgCl_2$ structures including the AgF_2 and $CuCl_2$ structure types as well as the novel $Ag(I)Cl(Cl_2)_{½}$ form. No such halogen-halogen interactions are observed in the corresponding AgF_2 and $CuCl_2$ compounds, which points to additional stabilizing effect of chlorine sublattice in combination with silver in these structures. We will discuss further only the separations between chlorine atoms that are not bonded to the same silver atom.

The shortest non-bonding Cl…Cl distance (2.823 Å) is calculated in the $Ag(I)Cl(Cl_2)_{½}$ polymorph. It corresponds to distance between a molecular chlorine and a Cl^- anion from a AgCl double-layer. The Cl_2 molecule forms two such short contacts with Cl^- anions belonging to two distinct AgCl double-layers located on opposite sides of the molecule. The Cl^- anions are arranged with the Cl_2 molecule in close to ideal linear arrangement, the angle (Cl-Cl… Cl^-) = 178° and the torsion angle (Cl^-…Cl-Cl… Cl^-) = 180°. This suggests presence of **type-II halogen interactions** $Cl^-…Cl_2$. They are known to form between halogen atoms with non-equivalent charge distribution (positive region on

the halogen atom in one interacting molecule and a negative halogen site on a second interacting unit) [J. Comput. Chem. 2019, 40, 1836–1860]. While the chlorine molecules are attached to the AgCl double-layers by extremely short Cl…Cl contacts, the Cl_2 molecules interact with each other by much longer Cl…Cl interactions, but these intermolecular distances are still considerably shorter (3.509 Å and 3.512 Å) than the tabulated van der Waals distance.

Second shortest Cl…Cl contacts are calculated for the lowest-energy ribbon $AgCl_2$ polymorph. They correspond to two shortest separations between the $AgCl_2$ ribbons stacked within the same layer (3.163 Å and 3.287 Å) and qualify as **type-I halogen interactions**. This can be concluded on the bases of the following observation: only one type of chlorine species with equal charge distribution is present in the structure (all $AgCl_2$ ribbons are structurally equivalent) and the interacting Ag-Cl…Cl angles depart considerably from linearity (162° and 165°, respectively). The type-I halogen interactions the most common halogen interactions in crystals. They are considered to be dispersion driven interactions that immerge as consequence of spatial restrictions and can be further influenced by other interactions [Varadwaj, J. Comput. Chem. 2019, 40, 1836–1860; Varadwaj, Inorganics **2019**, 7, 40]. In the ribbon $AgCl_2$ structure, type-I halogen interactions form an infinite zigzag network along direction of the propagation of the ribbons. While the in-plain $AgCl_2$ ribbons are held together by the short type-I halogen interactions, the ribbons from the neighbouring layers interact via longer van der Waals Cl…Cl contacts (3.544 Å). These features distinguish the $AgCl_2$ ribbon polymorph from the $CuCl_2$ crystal. Although both are formed by similar stacking of structurally same ribbons and thus possess similar topology of bonds and non-bonding Cl…Cl contacts, in the copper counterpart all non-bonding Cl…Cl distances are considerably larger (3.729 Å and 3.628 Å intra- and inter-layer distances, respectively) and comparable to weaker van der Waals contacts.

In the layered AgF_2 type polymorph, type-I intra- and inter-layer Cl…Cl interactions are present. The shortest intra- and inter-layer Cl…Cl separation are calculated to be shorter (3.383 Å and 3.379 Å) than sum of chlorine van der Waals radii. In respective experimentally confirmed AgF_2 compound, the corresponding inter-layer F…F separation (2.906 Å, ICSD6277) is comparable to the tabulated van der Waals distance (2.91 Å), while the intra-layer F…F distance (3.21 Å, ICSD6277) is considerably larger. Comparable values of the inter- and intra-layer F…F distances (2.844 and 3.115) were obtained also in our DFT+U+vdW calculations (the experimental and theoretical cell parameters agree within 1%). These results point to further stabilization of the layered structure due to presence of Cl…Cl interactions in comparison to its fluorine counterpart.

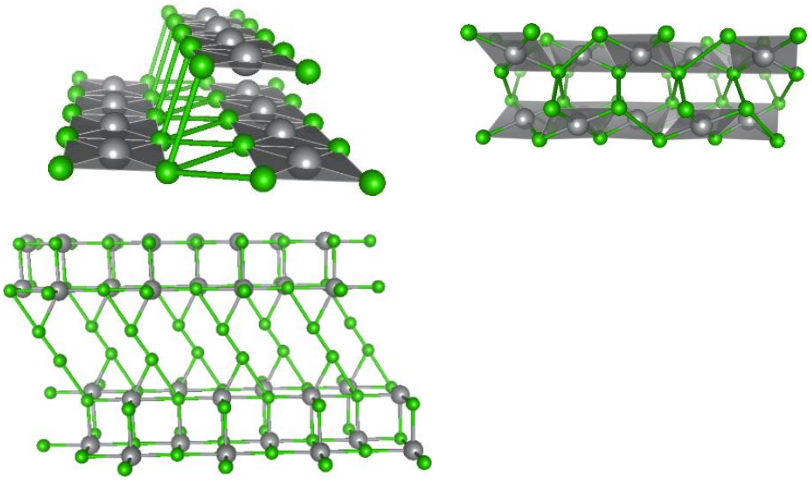

Figure S1. Fragments of three calculated $AgCl_2$ structures highlighting Cl…Cl contacts shorter than sum of the chlorine van der Waals radii (<3.62 Å): $CuCl_2$ type (left), AgF_2 type (middle), $Ag(I)Cl(Cl_2)_{½}$ (right).

In order to properly account for the Cl…Cl interactions, the description above and the Table below, have been presented in the electronic supplementary information, together with cif files for all important structures.

Table S1. Analysis of halogen…halogen distances and metal-halogen…halogen angels in the predicted $AgCl_2$ polymorphs (DFT+U+vdW results) and experimentally observed orthorhombic *P*bca AgF_2 (layers) and monoclinic *C*2m $CuCl_2$ structure (ribbons). Only distances shorter then sum of the van der Waals radii of the chlorine atoms are listed in case of the predicted $AgCl_2$ structures. *Tabulated* $d(Cl…Cl)^{vdW}$ = ***3.64 Å*** *and* $d(F…F)^{vdW}$ = ***2.92 Å*** *(webelements.com).*

Compound	Structure		d(Cl…Cl)/Å	<(M-Cl…Cl)/°
$AgCl_2$	Ribbon form	Intra-layer	3.163	162
			3.287	165
		Inter-layer	3.544	101
	AgF_2 type	Intra-layer	3.383	97
		Inter-layer	3.379	122, 153
			3.588	97
	$Ag(I)Cl(Cl_2)_{½}$	molecular	2.065	118
		$Cl_2…Cl^-$	2.823	88, 178$^{(Cl\text{-}Cl…Cl)}$
		$Cl_2…Cl_2$	3.509	
			3.512	
AgF_2	AgF_2(ICSD 6277)	Intra-layer	3.21	97
		Inter-layer	2.906	149
			2.972	117
$CuCl_2$	$CuCl_2$(ICSD 66645)	Intra-layer	3.729	133
		Inter-layer	3.628	95

S2. List of CIF files for predicted crystal structures of $AgCl_2$

Ribbon $AgCl_2$ (CdI_2 related), DFT+U+vdW

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_cell_angle_gamma 83.6468100000
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_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
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Cl1 Cl     2 i 0.22760 0.23568 0.58068 1.00000 Dx,Dy,Dz
Cl2 Cl     2 i 0.72709 0.23646 0.08252 1.00000 Dx,Dy,Dz
```

Layered $AgCl_2$ (ramsdellite related), DFT+U+vdW

```
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_cell_angle_gamma 90.0000000000
_cell_volume          266.7385928241

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3 -x,-y,-z
4 x,-y+1/2,z+1/2
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_atom_site_symmetry_multiplicity
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_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
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Cl1 Cl 4 e 0.56292 0.24782 -0.09039 1.00000 Dx,Dy,Dz
Cl2 Cl 4 e -0.00671 -0.00139 0.25204 1.00000 Dx,Dy,Dz

Layered AgF_2 type, DFT+U+vdW

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_cell_volume 251.2460146200

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4 -x+1/2,-y,z+1/2
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8 x+1/2,y,-z+1/2

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_atom_site_symmetry_multiplicity
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_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
Ag1 Ag     4 a 0.00000 0.00000 0.00000 1.00000 0,0,0
Cl1 Cl     8 c 0.16356 0.17339 0.37165 1.00000 Dx,Dy,Dz
```

Ag(I)[Cl(Cl_2)$_{½}$ (rocksalt AgCl layers), DFT+U+vdW

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_cell_angle_gamma 89.6266292959
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2 -x,-y,-z

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_atom_site_fract_x
_atom_site_fract_y
```

```
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
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Cl1 Cl     2 i 0.58131 0.58161 0.59377 1.00000 Dx,Dy,Dz
Cl2 Cl     2 i 0.79120 0.79271 0.85437 1.00000 Dx,Dy,Dz
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Ag(I)[Cl(Cl$_2$)$_{½}$ (hexagonal AgCl layers), DFT+U+vdW

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2 -x,-y,-z

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_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
Ag1 Ag     2 i 0.63593 0.77310 0.85641 1.00000 Dx,Dy,Dz
Cl1 Cl     2 i 0.44509 0.39171 0.59043 1.00000 Dx,Dy,Dz
Cl2 Cl     2 i 0.30901 0.12232 0.85165 1.00000 Dx,Dy,Dz
```

$AuCl_2$-type (disproportionated), hybrid DFT

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2 -x,-y,-z

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_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_fract_symmform
Ag1 Ag 2 i 0.25074 0.79761 0.15318 1.00000 Dx,Dy,Dz
Ag2 Ag 2 i 0.08529 0.25668 0.24133 1.00000 Dx,Dy,Dz
Cl1 Cl 2 i 0.25832 0.46630 0.38390 1.00000 Dx,Dy,Dz
Cl2 Cl 2 i 0.76631 0.10104 0.59556 1.00000 Dx,Dy,Dz
Cl3 Cl 2 i 0.74790 0.86709 0.07522 1.00000 Dx,Dy,Dz
Cl4 Cl 2 i 0.74306 0.31677 0.08934 1.00000 Dx,Dy,Dz