S1

ELECTRONIC SUPPLEMENTARY INFORMATION

The first example of a mixed valence ternary compound of silver with random distribution of Ag(I) and Ag(II) cations

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- S1. CIF file of $Ag_3(SbF_6)_4$ has been provided as a separate file.
- S2. CIF file of $K_2Ag(SbF_6)_4$ has been provided as a separate file.

S3. Photo of $Ag(SbF_6)_2$ solution in aHF.



Fig.S3: Solution of $Ag(SbF_6)_2$ in anhydrous hydrogen fluoride.



S4. Raman spectrum of impure blue-green Ag(SbF₆)₂.

Fig. S4: Raman spectrum of blue-green "Ag(SbF₆)₂" together with Raman spectra of AgSbF₆, Ag₃(SbF₆)₄ and Ag(SbF₆)₂.







Fig. S5: Self-supported homogeneous pellets (diameter 6 mm, thickness less than 1 mm) prepared from the pressed fine powder in a dry-box to prevent hydrolysis. They were inserted into specially designed FEP tubes equipped with PFA needle valves (Whitey Co., Swagelok Company). After argon has been pumped away, the tubes were sealed. The FEP tube containing the pellet was mounted on a sample holder in a vacuum chamber of the beam-line (photos are symbolic and they don't show silver fluoridoantimonates).

S5. Photos showing self-supported homogeneous pellets used for XANES spectroscopy.



S6. XRDP for a powder sample of $Ag_3(SbF_6)_4$.

Figure S6. X-ray diffraction pattern for a poweder sample of $Ag_3(SbF_6)_4$ containing small amount of $AgSbF_6$; $Ag(SbF_6)_2$ is absent.

S7. Raman spectra of Ag₃(SbF₆)₄ as compared to several relevant reference samples.



Figure S8. Raman spectra of $AgSbF_6$, $Ag_3(SbF_6)_4$ and $Ag(SbF_6)_2$.

The Raman spectrum of Ag₃(SbF₆)₄, together with Raman spectra of AgSbF₆ and Ag(SbF₆)₂ precursors, are shown in Figure S7; wavenumbers are given in Table S1. The spectra exhibit vibrational bands which belong mainly to anionic part of the compounds, *i.e.* SbF₆⁻ groups. The strongest Raman bands at 664 cm⁻¹ may be assigned to symmetric stretching (v_1) mode and the weak ones at 584 cm⁻¹ and 291/268 cm⁻¹ to v_2 (SbF₆) and to bending (v_5) mode, respectively. The remaining weak band at 494 cm⁻¹ is in the region typical for Sb–F_b–M stretching modes (*i.e.* species where one fluorine bridges two different atoms),^{S1} and can be readily assigned to Ag–F_b–Sb stretching modes. Such bands are always observed in the case of Ag(II) salts, *i.e.* in Ag(SbF₆)₂^{S1} and [IF₆][Ag(SbF₆)₃]^{S2} two such bands are observed (530 / 448 cm⁻¹ and 488 / 449 cm⁻¹, respectively). The Ag(II) cation is known to exert high polarizing power and is sustained only by anions which are stable to loss of F⁻ and of e⁻.^{S3} Ag(II) is capable of partially withdrawing F⁻ from the SbF₆⁻ (which is one of the poorest F⁻ donors known). Similar features are seen also in the Raman spectra of Ag(SbF₆)₂; the presence of bands around 500 cm⁻¹ confirms strong interactions between cation and anion *via* fluorine bridge, consistent with the presence of highly distorted SbF₆ octahedra in the crystal structure of this

compound. Such bands are <u>not</u> observed in the case of $AgSbF_6$ salt which contains Ag(I) cations of a much lower polarizing power. The vibrational band at 494 cm⁻¹ in the Raman spectrum of $Ag_3(SbF_6)_4$ may therefore assigned be to $Ag(II)-F_b-Sb$ bridging and is in agreement with presence of Ag(II) cations in $Ag_3(SbF_6)_4$.

| AgSbF ₆ | $Ag_3(SbF_6)_4$ | $Ag(SbF_6)_2^a$ | $[IF_6][Ag(SbF_6)_3]$ | assign ^b |
|--------------------|-------------------------|-----------------|-----------------------|--------------------------------------|
| | | 718(60) | | v_3 (SbF ₆) |
| | | 694(20) | | v_3 (SbF ₆) |
| | | 687(15) | 680(9) | v_3 (SbF ₆) |
| 657(100) | 664(100) | 647(100) | 654(95) | v ₁ (SbF ₆) |
| 562(10) | 584(10,br) ^c | | 559(10) | v ₂ (SbF ₆) |
| | 494(5,br) | 530(5) | 488(sh) | v(Sb–F _b) |
| | | 448(15) | 449(7) | v(Sb–F _b) |
| | | 335(5) | | v ₄ (SbF ₆) ? |
| | | 315(2) | | v ₄ (SbF ₆) ? |
| | 291(10) | 284(sh) | 294(sh) | <i>v</i> ₅(SbF ₆) |
| | 268(sh) | 273(45) | 280(38) | v₅(SbF ₆) |
| 228(20) | | 256(25) | | v_5 (SbF ₆) |
| | | 200(5) | | |

Table S1: Raman shifts $[cm^{-1}]$ detected for Ag₃(SbF₆)₄ together with literature data for AgSbF₆, Ag(SbF₆)₂ and $[IF_6][Ag(SbF_6)_3]$.^{S1,S2,S4}

^aRaman spectrum of Ag(SbF₆)₂ was first reported in Ref.^{S5} and reinvestigated later in Ref.^{S1}. Since in the first report the strongest band was observed at 668 cm⁻¹, it seems that Ag(SbF₆)₂ was partly decomposed to Ag₃(SbF₆)₄. ^bAssignments of the modes of [SbF₆]⁻ are for idealized octahedral symmetry although in the solid state the actual local symmetry is lower. ^cSymbols denote shoulder (sh) and broad (br).



S8. FIR and MIR absorption spectra for $Ag_3(SbF_6)_4$, $Ag(SbF_6)_2$, and $AgSbF_6$.

Fig.S8 FTIR spectra of $AgSbF_{6}$, $Ag_3(SbF_6)_4$ and $Ag(SbF_6)_2$.

Table S2: Wavenumbers of IR absorption bands $[cm^{-1}]$ detected for $Ag_3(SbF_6)_4$ together with those measured for $AgSbF_6$ and $Ag(SbF_6)_2$.

| AgSbF ₆ | $Ag(SbF_6)_2$ | $Ag_3(SbF_6)_4$ | Assignment ^a |
|--------------------|---------------|-----------------|---------------------------|
| 833 (vw) | | | terminal SbF_3 |
| | 724 (sh) | | |
| | 690 (vs) | | |
| 669 (s, br) | | 660 (s, br) | |
| | | | |
| | 648 (s) | | bridging SbF ₃ |
| 590 (sh) | | | |
| | 551 (s) | 555 (sh) | |
| | | 518 (s, br) | |
| | 495 (s) | | |
| | | 410 (sh) | |
| | | | |
| 396 (m) | | | Sb-F str |
| | 221 () | | Ch E dof |
| 211(m) | 331 (VW) | 212 () | SD-F dei |
| 311 (m) | 312 (SN) | 312 (W) | |
| 282 (s) | 275 (m) | 282 (s) | |
| 263 (m) | 226 () | 264 (S) | |
| | 236 (m) | 222 () | |
| 202 (-) | | 222 (m) | lattice modes |
| 203 (s) | | | |
| 183 (s) | | 183 (sh) | |
| | | 123 (vw) | |
| 105 (m) | | 103 (sh) | |
| 84 (s) | 85 (w) | 82 (w) | |

^a from Ref.^{S6}.

S9. Comparison of magnetic properties of Ag₃(SbF₆)₄ and Ag(SbF₆)₂.

To compare the magnetic properties of $Ag_3(SbF_6)_4$ with $Ag(SbF_6)_2$, where Ag^{2+} ions are also isolated between each other by bulky diamagnetic SbF_6 groups, magnetic investigations of $Ag(SbF_6)_2$ have also been done. Previously reported results of magnetic properties of $Ag(SbF_6)_2$ were done only in 3–65 K temperature range and on impure samples.

Ag(SbF₆)₂ crystallizes is the Ni(SbF₆)₂-type where M^{2+} cations are sixfold co-ordinated by fluorine atoms. MF_6 octahedra share fluorine atoms with six XF_6 units on either side of the plane formed by the *M* atoms forming slabs. Ag²⁺ occupies an elongated octahedral site at a center of symmetry, in an approximately close-packed fluorine ligand array provided by SbF₆⁻ groups.

The variation of the magnetization of $Ag(SbF_6)_2$ at T = 5 K and 20 K (Figure S12) is linear with the magnetic field up to 5 T. The zero-field cooled (ZFC) and field cooled (FC) magnetic susceptibilities of Ag(SbF₆)₂ overlap at all temperatures and show a maximum at 12 K, thus exhibiting an unexpected antiferromagnetic departure from Curie law behaviour with a Neél temperature of 12 K, indicating long-range antiferromagnetic interactions within the layers. In isostructural gold compound (i.e. $Au(SbF_6)_2$) the same phenomenon has been observed. This conclusion is consistent with the negative value of θ_p (-14 K) obtained by fitting the high-temperature portion (T > 100 K) of the susceptibility data to a Curie-Weiss law. The fitted Curie constant C = 0.5 emu K mol⁻¹ (μ_{eff} = 2 B.M.) is close to the localized electron, spin-only value, expected for a Ag(II) (d⁹) cation and in agreement with structural arrangement where discrete Ag(II) are separated by closed-shell SbF_6^- anions. Similar values were observed in isostructural Ag(BiF₆)₂ and Ag(TaF₆)₂ where their magnetic susceptibilities obey the Curie-Weiss law for a wide temperature range $[Ag(BiF_6)_2: 35-280 \text{ K}, Ag(TaF_6)_2: \text{ down to } 13 \text{ K}]$ and have an effective magnetic moments μ_{eff} = 2.1 B.M. (Ag(BiF₆)₂; room temperature), 1.95 B.M. (Ag(TaF₆)₂ at 251 K) and 1.90 B.M. (Ag(TaF₆)₂; 13 K). The calculated θ of Ag(TaF₆)₂ equals to 3.1(±1.1) K. The increase of magnetic susceptibility of $Ag(SbF_6)_2$ (Figure) at temperature below 4 K is very probable caused by an unknown magnetic impurity or just by some uncoupled Ag²⁺ ions.



Fig.S9 Temperature dependent susceptibility $\chi(T)$ of Ag(SbF₆)₂ in low temperature region measured in H = 1000 Oe. For higher temperatures the susceptibility follows Curie-Weiss law as can be seen from inverse susceptibility χ^1 vs. T graph (inset). The full line in inset is a fit to Equation S1.

A "shallow maximum" in the temperature dependent susceptibility has been already observed by M. S. R. Cader *et al.*⁵⁶ Our experimental data reveal a well pronounced maximum at $T_{max} = 11.7$ K indicating an antiferromagnetic interaction between Ag(II) ions in the layers of Ag(SbF₆)₂. In order to estimate a spin exchange interaction J between the nearest neighbours we apply a model proposed by G. A. Baker and H. E. Gilbert^{S7} for a two-dimensional square lattice. The measured susceptibility was fitted with the function^{S7} for T > 20 K (Eq. S1):

$$\chi = \frac{N_A g^2 \mu_B^2}{4k_B T} (1 + \sum_{n \ge 1} \frac{\alpha_n}{2^n n!} x^n),$$
 (Eq.S1)

Where N_A is the Avogadro number, g gyromagnetic factor, μ_B the Bohr magneton, k_B the Boltzmann constant and $\chi = J / (k_B \cdot T)$. The coefficients α_n were used as described in Ref.S7. The best fit was obtained using spin exchange interaction $J/k_B = -7.0$ K and is shown as a full line in the inset in Figure S9.



Fig.S10. M vs. H curves at 2 K , 5 K and 20 K for Ag(SbF₆)₂



S11. NUV absorption spectra for Ag₃(SbF₆)₄, Ag(SbF₆)₂ and AgSbF₆.

Fig.S11. NUV absorption spectra for $Ag_3(SbF_6)_4$, $Ag(SbF_6)_2$ and $AgSbF_6$.

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