Inorg. Chem. **2008**, *47*, 4209−4214

Inorganic Chemistry

Article

Synthesis, Raman Spectra and Crystal Structures of $[Cu(XeF_2)_n](SbF_6)_2$ ($n = 2, 4$)

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Received November 15, 2007

Pure $[Cu(XeF_2)_2](SbF_6)_2$ was prepared by the reaction of $Cu(SbF_6)_2$ with a stoichiometric amount of XeF_2 in anhydrous hydrogen fluoride (aHF) at ambient temperature. The reaction between $Cu(SbF_6)_2$ and XeF_2 (1:4 molar ratio) in aHF yielded $[Cu(XeF_2)_4](SbF_6)_2$ contaminated with traces of $Xe_2F_3SbF_6$ and CuF_2. The 6-fold coordination of Cu^{2+} in $[Cu(XeF_2)_2](SbF_6)_2$ includes two fluorine atoms from two XeF_2 ligands and four fluorine atoms provided by four $[SbF_6]^-$ anions. The neighboring $[Cu(XeF_2)_2]^{2+}$ moieties are connected via two $[SbF_6]$ units, with the bridging fluorine atoms in cis positions, into infinite $-[Cu(\eta^1\text{-}XeF_2)_2]-(cis\text{-}\eta^2\text{-}SbF_6)_2-[Cu(\eta^1\text{-}XeF_2)_2]-$ chains. Because of the high electron affinity of Cu^{2+}, coordinated XeF_2 shows the highest distortion ($Xe-F_b = 210.2(5)$ pm, $Xe-F_t = 190.6(5)$ pm) observed so far among all known $[M^{x+}(XeF_2)_n](A)_x$ (A = BF_4, PF_6, etc.) complexes. The four equatorial coordination sites of the Cu^{2+} ion in $[Cu(XeF_2)_4](SbF_6)_2$ are occupied by four XeF_2 ligands. Two fluorine atoms belonging to two $[SbF_6]$ units complete the Cu^{2+} coordination environment. The neighboring $[Cu(XeF_2)_4]^{2+}$ species are linked via one $[SbF_6]$ unit, with bridging fluorine atoms in trans positions, into linear infinite $-[Cu(\eta^1\text{-}XeF_2)_4]-(trans\text{-}\eta^2\text{-}SbF_6)-[Cu(\eta^1\text{-}XeF_2)_4]-$ chains. To compensate for the remaining positive charge, crystallographically independent $[SbF_6]^-$ anions are located between the chains and are fixed in the crystal space by weak $Xe\cdots F(Sb)$ interactions.

Introduction

Recently, the crystal structures of $[M(XeF_2)_6](SbF_6)_2$ (M = Cu, Zn) were reported.[1] The crystal structures consist of isolated homoleptic $[M(XeF_2)_6]^{2+}$ cations and $[SbF_6]^-$ anions. Attempts to prepare larger amounts of pure compounds were unsuccessful because the reaction between $M(SbF_6)_2$ and XeF_2 in the molar ratio 1:6 always resulted in a mixture of $[M(XeF_2)_6](SbF_6)_2$, $Xe_2F_3SbF_6$, and MF_2. Additionally, some of the Raman spectra recorded during these investigations indicate that other phases could exist in the $M(SbF_6)_2/XeF_2$ (M = Cu, Zn) systems. Because compounds of the type $[M(XeF_2)_n](XF_6)_2$ (X = As, Sb), with $n = 4$ and 2, are known for the Mg^{2+} cation,[2] which is similar in size (8.6 pm, C.N. = 6)[3] to Cu^{2+} (8.7 pm for C.N. = 6),[3] the study of the $Cu(SbF_6)_2/XeF_2$ system has been extended. Two new phases $-[Cu(XeF_2)_n](SbF_6)_2-$ with lower XeF_2 content ($n = 4, 2$) were prepared. Their syntheses, crystal structures, Raman spectra, and their comparisons with $[Cu(XeF_2)_6](SbF_6)_2$[1] are described in the present article.

Experimental Section

Caution! *Anhydrous HF and some fluorides are highly toxic and must be handled using appropriate apparatus and protective gear.*

Apparatus and Reagents. Volatile materials (SbF_5, aHF) were handled in an all-Teflon vacuum line equipped with Teflon valves. The manipulation of the nonvolatile materials was done in a dry box (M. Braun). The residual water in the atmosphere within the dry box never exceeded 2 ppm. The reactions were carried out in FEP (tetrafluoroethylene-hexafluoropropylene) reaction vessels (length 250−300 mm, i.d. 15.5 mm, o.d. 18.75 mm) equipped with Teflon valves and Teflon coated stirring bars. Prior to use, all reaction vessels were passivated with elemental fluorine. Fluorine was used as supplied (Solvay). Anhydrous HF (Fluka, Purum) was treated with K_2NiF_6 (Ozark Mahoning) for several hours prior to use. The compound, $Cu(SbF_6)_2$, was synthesized by reaction between CuF_2, $2SbF_3$, and elemental fluorine as previously de-

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10.1021/ic702249u CCC: $40.75

Table 1. Crystal Data and Structure Refinement for $[Cu(XeF_2)_2](SbF_6)_2$ and $[Cu(XeF_2)_4](SbF_6)_2$

chem formula	$[Cu(XeF_2)_2](SbF_6)_2$	$[Cu(XeF_2)_4](SbF_6)_2$
space group	$P2_1/c$	$\bar{I}4$
a (pm)	558.28(19)	1108.9(7)
b (pm)	1474.1(5)	1108.9(7)
c (pm)	911.8(3)	827.8(6)
β (deg)	90.982(3)	
V (nm^3)	0.7502(4)	1.0178(12)
Z	2	2
fw (g mol^{-1})	873.64	1212.23
D_{calcd} (g cm^{-3})	3.867	3.955
T (K)	200	200
μ (mm^{-1})	9.577	10.377
R1[a]	0.0473	0.0185
wR2 ($I > 2.00\ \sigma(I)$)[b]	0.1192	0.0397

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [b] $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2/\Sigma(w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Lengths (pm) and Bond Angles (deg) in $[Cu(XeF_2)_4](SbF_6)_2$

4 × Cu1−F2	192.0(3)	Xe1−F3	193.9(4)
2 × Cu1−F1	223.4(5)	Xe1−F2	209.4(3)
4 × Sb1−F11	185.2(4)		
2 × Sb1−F1	190.5(5)	Cu1−F1−Sb1	180.0
4 × Sb2−F22	186.0(4)	Cu1−F2−Xe1	127.8(2)
2 × Sb2−F21	186.2(5)	F2−Xe1−F3	177.0(2)

Table 3. Selected Bond Lengths (pm) and Bond Angles (deg) in $[Cu(XeF_2)_2](SbF_6)_2$

2 × Cu1−F1	185.7(5)	Sb1−F15	184.3(6)
2 × Cu1−F11	209.0(5)	Sb1−F16	184.1(6)
2 × Cu1−F12	212.3(5)	Xe1−F2	190.6(5)
		Xe1−F1	210.2(5)
Sb1−F11	191.7(5)		
Sb1−F12	189.1(5)	Cu1−F12−Sb1	140.7(3)
Sb1−F13	186.1(6)	Cu1−F1−Xe1	170.0(3)
Sb1−F14	187.0(6)	F1−Xe1−F2	178.3(3)

scribed.[4] Xenon difluoride was prepared by a photochemical reaction between xenon and F_2 at ambient temperature.[5]

Raman Spectroscopy. Raman spectra with a resolution of 1 cm^{-1} were recorded (10−20 scans) on a Renishaw Raman Imaging Microscope System 1000 using the 632.8 nm exciting line of a He−Ne laser.

X-ray powder diffraction patterns were obtained using the Debye−Scherrer technique with nickel-filtered Cu Kα radiation. Samples were loaded into quartz capillaries (0.3 mm) in a dry box. Intensities were estimated visually.

Synthesis of $[Cu(XeF_2)_n](SbF_6)_2$ (n = 2, 4). A mixture of $Cu(SbF_6)_2$ (0.56 mmol) and XeF_2 (1.12 and 2.24 mmol, respectively) was loaded in a reaction vessel in a dry box. Anhydrous HF (4 mL) was condensed onto the reaction mixture, and the reaction vessel was warmed to ambient temperature. When the $n(Cu(SbF_6)_2)/n(XeF_2)$ molar ratio was equal to 1:2, a clear colorless solution was obtained. In the case of a 1:4 molar ratio, traces of white insoluble solid were observed. After 2 h of intense stirring, the volatiles were pumped off at ambient temperature (in the case of $[Cu(XeF_2)_4](SbF_6)_2$, the pumping was stopped when a 1:4 mol ratio between copper and XeF_2 was reached). Powdered products were obtained. The final masses of the isolated solids were: 0.491 mg (Calcd for $[Cu(XeF_2)_2](SbF_6)_2$, 0.469 mg); 0.675 mg (Calcd for $[Cu(XeF_2)_4](SbF_6)_2$, 0.680 mg). The later is not stable under dynamic vacuum at ambient temperature and slowly loses mass (approximately 10 mg of XeF_2 per hour per mmol of copper). In another experiment, the product of reaction between $Cu(SbF_6)_2)$ and XeF_2 (molar ratio 1:4) had been pumped on until the mass versus time remained constant. Raman spectra of the remaining solid confirmed the presence of $[Cu(XeF_2)_2](SbF_6)_2$, whereas no $[Cu(XeF_2)_4](SbF_6)_2$ could be detected. Reactions were later repeated in the same manner, and the products were isolated at 243 K. Large single crystals of $[Cu(XeF_2)_n](SbF_6)_2$ (n = 4, 2) were recovered as colorless blocks during the isolation. Raman spectra were recorded, X-ray powder diffraction photos were taken, and chemical analyses were obtained: $[Cu(XeF_2)_2](SbF_6)_2$: Calcd: copper, 7.27; fluorine 34.80; antimony, 27.87; found: copper, 7.2; fluorine, 33.5; antimony, 27.1 (corresponding to molar ratio: $n(Cu)/n(Sb)/n(F) = 1.0{:}\ 2.04{:}\ 15.6$). $[Cu(XeF_2)_4](SbF_6)_2$: Calcd: copper, 5.24; fluorine, 31.35; antimony, 20.09; found: copper, 5.1; fluorine, 30.7; antimony, 19.7 (corresponding to molar ratio: $n(Cu)/n(Sb)/n(F) = 1.0{:}2.02{:}20.1$). The results of chemical analyses are given in mass percents.

Crystal Structure Determination. Crystals were immersed in perfluorinated oil (ABCR, FO5960) in the dry box, selected under a microscope, and transferred into the cold nitrogen stream of the diffractometer. Data were collected on Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector using graphite monochromated Mo Kα radiation at 200 K. The data were corrected for Lorentz and polarization effects. A multiscan absorption correction was applied to all data sets. Both structures were solved by direct methods using the SIR-92[6] program (program package TeXsan) and refined with *SHELXL-97*[7] software, implemented in the program package *WinGX*.[8] The figures were prepared using *DIAMOND 3.1* software.[9] The crystal data and the details of structure refinement are given in Table 1, and selected distances and angles are given in Tables 2 and 3, respectively.

Chemical Analyses. The total fluoride (F) amount was determined after complete reductive decomposition of the sample.[10–12] The amount of antimony was determined by redox titration after prior reduction,[13,14] whereas the amount of copper was determined by complexometric titration.[15]

Results and Discussion

Synthesis. The reaction between $Cu(SbF_6)_2$ and a stoichiometric amount of XeF_2 in anhydrous hydrogen fluoride (aHF) yields a clear, colorless solution from which pure $[Cu(XeF_2)_2](SbF_6)_2$ could be isolated (eq 1):

$$Cu(SuF_6)_2 + 2XeF_2 \xrightarrow[298K]{aHF} [Cu(XeF_2)_2](SbF_6)_2 \qquad (1)$$

When isolation was done at ambient temperature, powdered $[Cu(XeF_2)_2](SbF_6)_2$ was obtained. Cooling of the solution to 243 K followed by removal of volatiles at the same temperature resulted in large block-shaped single crystals.

When the starting ratio $n(Cu(SbF_6)_2)/n(XeF_2)$ was 1:4, traces of insoluble white solid were observed in the clear colorless solution. Besides $[Cu(XeF_2)_4](SbF_6)_2$, some $Xe_2F_3SbF_6$ formed along with CuF_2 precipitate (eq 2):

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$$Cu(SbF_6)_2 + 4XeF_2 \xrightarrow[298K]{aHF} x[Cu(XeF_2)_4](SbF_6)_2 + (2-2x)Xe_2F_3SbF_6 + (1-x)CuF_2 \quad (2)$$

Although the chemical analyses of the product isolated at 243 K were in accordance with $[Cu(XeF_2)_4](SbF_6)_2$, formation (Experimental Section) and X-ray powder diffraction photos did not indicate the presence of other phases and Raman spectroscopy showed that, besides $[Cu(XeF_2)_4](SbF_6)_2$, traces of $Xe_2F_3SbF_6$ were also present. This is in agreement with previous studies where it was found that two competitive reactions are in equilibrium in the $Cu(SbF_6)_2$—XeF_2 system.[1] The first is the formation of $[Cu(XeF_2)_n](SbF_6)_2$ (where $n = 6$ or 4, depending on the initial $Cu(SbF_6)_2/XeF_2$ ratio), and second is the formation of $Xe_2F_3SbF_6$ accompanied by precipitation of CuF_2. The fluoride ion donor strenghts of CuF_2 and XeF_2 toward the strong fluoro-acceptor SbF_5 are nearly equal (more details about the importance of fluoride ion donor strengths for preparation of XeF_2 complexes can be found in the literature[16,17]). With increasing amounts of XeF_2 with respect to $Cu(SbF_6)_2$, the equilibrium is shifted toward $Xe_2F_3SbF_6$. In such cases, it is unlikely that $Xe_2F_3SbF_6$ can be completely avoided when the starting ratio $n(XeF_2)/n(Cu(SbF_6)_2) > 2$. This finding is supported by the reported synthesis of $Ba(SbF_6)_2 \cdot 5XeF_2$,[18] where BaF_2 is known to be a much better fluoride ion donor (fluoro-base) than CuF_2. The synthesis of pure $Ba(SbF_6)_2 \cdot 5XeF_2$ was claimed to result from the reaction between $Ba(SbF_6)_2$ and XeF_2 (1:12 starting molar ratio) in aHF. However, a split band (581/592 cm^{-1}) typical of the $Xe_2F_3^+$ cation ($Xe_2F_3SbF_6$) is clearly visible in the Raman spectrum. In the same report,[18] this split band has been erroneously assigned to the slighlty distorted $[SbF_6]^-$ anion Table 4.

As in the case for $[Mg(XeF_2)_4](AsF_6)_2$, $[Cu(XeF_2)_4](SbF_6)_2$is not stable under dynamic vacuum at ambient temperature. Removal of XeF_2 from $[Cu(XeF_2)_4](SbF_6)_2$ results in $[Cu(XeF_2)_2](SbF_6)_2$.

X-ray Crystal Structures of $[Cu(XeF_2)_4](SbF_6)_2$ and $[Cu(XeF_2)_2](SbF_6)_2$. Details of data collection parameters and other crystallographic information are given in Table 1. Important bond lengths and bond angles are listed in Tables 2 and 3.

The copper atom in the crystal structure of $[Cu(XeF_2)_4](SbF_6)_2$, is found in an usual elongated octahedral coordination geometry (4 + 2) consisting of six fluorine atoms (Figure 1).

Four fluorine contacts are provided by four XeF_2 molecules (Cu−F(Xe) = 4 × 192.0(3) pm). The remaining two contacts are in *trans* positions and belong to bridging $[SbF_6]$ units (Cu−F(Sb) = 2 × 223.4(5) pm), completing the Cu^{2+} coordination environment. The structure of $[Cu(XeF_2)_4](SbF_6)_2$ consists of linear infinite $-[Cu(\eta^1\text{-}XeF_2)_4]-(trans\text{-}\eta^2\text{-}SbF_6)-[Cu(\eta^1\text{-}XeF_2)_4]-$ chains where the $[CuF_6]$ and $[SbF_6]$ octahedra sharing joint apexes that alternate along the *c*- axis of the unit cell (Figure 1). The free $[SbF_6]^-$ anions are located between chains (Figure 2) and are fixed in the crystal lattice by weak Xe···F interactions (Xe···*F* = 316 pm). The Sb−F distances are equal to 185.2(4) pm for the terminal and 190.5(5) pm for the bridging fluorine atoms of the bridging $[SbF_6]^-$ anion and are 186.0(4)−186.2(5) pm in the isolated $[SbF_6]^-$ anions.

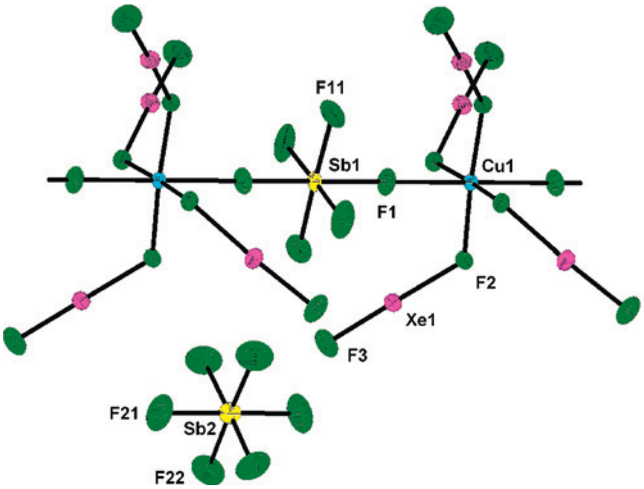

Figure 1. Part of the crystal structure of $[Cu(XeF_2)_4](SbF_6)_2$.

Whereas the structures of $[Cu(XeF_2)_4](SbF_6)_2$ and $[Mg(XeF_2)_4](SbF_6)_2$ differ, the structure of $[Cu(XeF_2)_2](SbF_6)_2]$ is closely related to that of $[Mg(XeF_2)_2](AsF_6)_2$. The Cu^{2+} cation is coordinated to two XeF_2 molecules with Cu−F(Xe) distances of 185.7(5) pm. The 6-fold coordination of Cu^{2+} is completed by four fluorine atoms provided by four $[SbF_6]$ units (Figure 3). The Cu−F(Sb) distances are 2 × 209.0(5) pm and 2 × 212.3(5) pm. Thus, the Cu^{2+} cation is found in a rarely observed, compressed 2 + 4 octahedral coordination environment. The neighboring $[Cu(XeF_2)_2]^{2+}$ moieties are linked via two $[SbF_6]^-$ units, with bridging fluorine atoms in cis positions, into infinite $-[Cu(\eta^1\text{-}XeF_2)_2]-(cis\text{-}\eta^2\text{-}SbF_6)_2-[Cu(\eta^1\text{-}XeF_2)_2]-$ chains that are parallel to the *a* axis (Figure 3). These chains are interconnected by weak Xe···F(Sb) contacts (314− 333 pm) forming a 3D network (Figure 4). Chain formation and their packing in the crystal structure of $[Cu(XeF_2)_2](SbF_6)_2$ has the same characteristics as in $[Mg(XeF_2)_2](AsF_6)_2$.[2] Unlike the former, the magnesium compound has been reported to crystallize in a higher orthorhombic symmetry (space group *Pban*, No. 55). The orthorhombic phase of $[Mg(XeF_2)_2](AsF_6)_2$ was described as a high-temperature phase, whereas the crystal structure of the low-temperature phase remains unknown. The main differences between the structures are the values of Xe−F−M (M = Mg, Cu) angles, which are nearly linear (177.5(3)°) for the magnesium derivative and kinked (170.0(3)°) for the copper derivative.

The Sb−F distances in $[Cu(XeF_2)_2](SbF_6)_2$ are in the range 184.1(6)−187.0(6) pm for terminal and 189.1(5)−191.7(5) pm for the bridging fluorine atoms.

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Table 4. Raman Spectra of $[Cu(XeF_2)_4](SbF_6)_2$ and $[Cu(XeF_2)_4](SbF_6)_2$

$[Cu(XeF_2)_2](SbF_6)_2$	$[Cu(XeF_2)_4](SbF_6)_2$	assign[a]
684(11)		$\nu_3(SbF_6)$
652(35)	655(23)	$\nu_1(SbF_6)$
	644(24)	ν_1(free SbF_6)
591(70, sh)[b]	578(60)	$\nu(Xe-F)$
582(100)	562(100)	$\nu(Xe-F)$
492(4, vbr)[b]	486(8)	$\nu(Sb-F_b)$
	407(6)	$\nu(Xe-F_b)$
	364(8)	$\nu(Cu\cdots FSb)$
	307(7)	$\nu_4(SbF_6)$
284(17)		$\nu_5(SbF_6)$
280(17)	277(11)	$\nu_5(SbF_6)$
200(3)	195(6)	$\delta(XeF_2)/\delta(SbFCu)$
	155(sh)	$\delta(XeF_2)/\delta(SbFCu)$
	148(11)	$\delta(XeF_2)/\delta(SbFCu)$

[a] Assignments of $[SbF_6]^-$ are made for octahedral symmetry, although in the solid state the actual symmetry is lower. [b] Symbols denote shoulder (sh) and very broad (vbr).

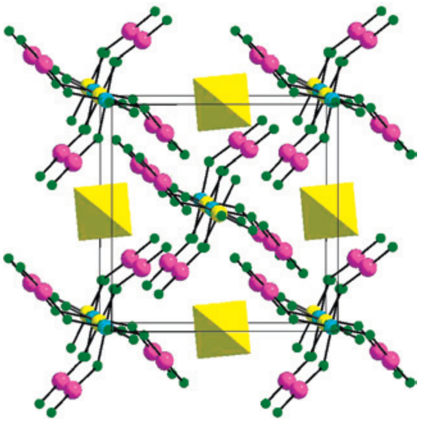

Figure 2. Packing of $-[Cu(XeF_2)_4]-[SbF_6]-[Cu(XeF_2)_4]-$ chains and free $[SbF_6]$ units in the crystal structure of $[Cu(XeF_2)_4](SbF_6)_2$.

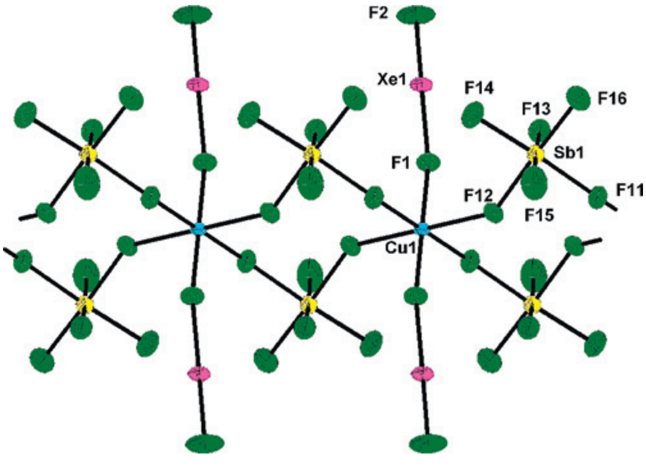

Figure 3. Part of the crystal structure of $[Cu(XeF_2)_2](SbF_6)_2$.

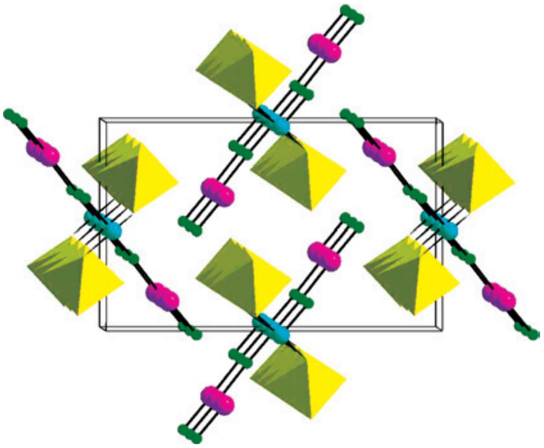

Figure 4. Packing of the $-[Cu(XeF_2)_2]-(SbF_6)_2-[Cu(XeF_2)_2]-$ chains in the crystal structure of $[Cu(XeF_2)_2](SbF_6)_2$.

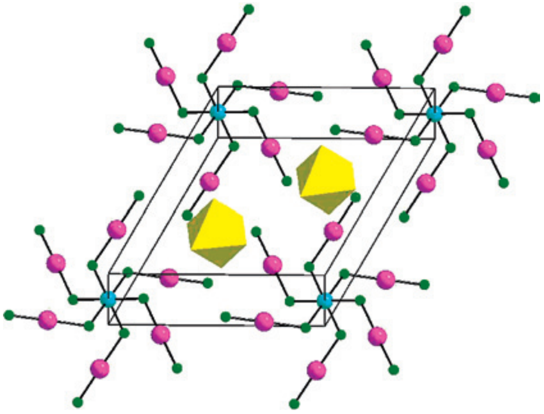

Figure 5. A portion of the crystal structure of $[Cu(XeF_2)_6](SbF_6)_2$ consisting of $[Cu(XeF_2)_6]^{2+}$ cations and $[SbF_6]^-$ anions.

Correlations among $[Cu(XeF_2)_2](SbF_6)_n$ (n = 6, 4, 2) Compounds. The structure of the previously reported $[Cu(XeF_2)_6](SbF_6)_2$[1] is of an ionic type because it consists of isolated homoleptic $[Cu(XeF_2)_6]^{2+}$ cations and $[SbF_6]^-$ anions held together by weak $Xe\cdots F$ contacts (Figure 5).

As explained in the first paragraph of the Discussion, $[Cu(XeF_2)_6](SbF_6)_2$ could not be prepared in a pure form. Its preparations always resulted in a mixture of $[Cu(XeF_2)_6](SbF_6)_2$, $Xe_2F_3SbF_6$, and CuF_2. Because the vibrational bands of $Xe_2F_3SbF_6$ coincide with the vibrational bands of $[Cu(XeF_2)_n](SbF_6)_2$ (n = 6, 4, 2; next paragraph and ref 1), the decomposition path of $[Cu(XeF_2)_6](SbF_6)_2$ could not be monitored by Raman spectroscopy. However, on the basis of the crystal structures of $[Cu(XeF_2)_2](SbF_6)_2$ (n = 6, 4, 2), a two-step decomposition could be inferred: In the first step, the loss of two XeF_2 (in trans position) per $[Cu(XeF_2)_6](SbF_6)_2$ is compensated by the interaction of neighboring $[Cu(XeF_2)_4]^{2+}$ moieties with two $[SbF_6]$ units in a trans arrangement. Infinite chains of alternating $[Cu(XeF_2)_4]^{2+}$ moieties and $[SbF_6]$ units are formed in this manner, whereas one $[SbF_6]^-$ anion remains free (Figure 1). In a second step, removal of two more XeF_2 molecules (in trans positions) per $[Cu(XeF_2)_4](SbF_6)_2$ is repeated, and the free $[SbF_6]$ unit becomes involved in coordination. Simultaneously, rearrangement of the bridged *trans*-η^2-SbF_6 anion to *cis*-η^2-SbF_6 occurs. Two neighboring $[Cu(XeF_2)_2]^{2+}$ species are now bridged by two $[SbF_6]$ units (Figure 3).

In all three compounds, copper is 6-fold coordinated to fluorine atoms. In $[Cu(XeF_2)_6](SbF_6)_2$, all six $Cu-F(Xe)$ bond lengths are equal to 197.9(3) pm (most likely the result of static or dynamic Jahn–Teller effects). Hexacoordinate Cu^{2+} in $[Cu(XeF_2)_4](SbF_6)_2$ exhibits the usual Jahn–Teller 4 + 2 distortion with tetragonal elongation along the 4-fold axis ($Cu-F(Xe) = 4 \times 192.0(3)$ pm; $Cu-F(Sb)$ 2 × 223.4 pm); meanwhile Cu^{2+} in $[Cu(XeF_2)_2](SbF_6)_2$ is found in the rarely observed, compressed 2 + 4 octahedral geometry

(Cu−F(Xe) = 2 × 185.7(5) pm; Cu−F(Sb) = 2 × 209.0(5)/2 × 212.3(5) pm). The shortest Cu−F bonds (183.8 pm) were previously observed only in the infinite $[CuF_5]_n^{3n-}$ chains comprised of $[CuF_6]^{4-}$ octahedra in the crystal structure of $CuFAsF_6$.[19] For comparison, CuF_2 displays the usual elongated Jahn−Teller distortion with Cu−F distances in the range 191.0−203.5 pm.[19]

The Cu−F(Xe) bond lengths decrease with the decreasing number of XeF_2 ligands bound to the copper atom due to the lower nucleophilicity of $[SbF_6]$ (i.e., $[SbF_6]^-$ is a poor Lewis base)[17] when compared with that of XeF_2. The steric factors such as repulsions between the lone pairs of XeF_2 ligands could be excluded because $[SbF_6]^-$ anions have larger volumes ($0.121\ nm^3$)[20] than XeF_2 molecules ($0.065\ nm^{3\,21}$).

The decrease in the Cu−F(Xe) bond lengths in $[Cu(XeF_2)_n](SbF_6)_2$ ($n = 6$: 197.9(3) pm, $n = 4$: 192.0(3) pm, $n = 2$: 185.7(5) pm) correlate with the increase of $Xe-F_b$ ($n = 6$: 208.3(3) pm, $n = 4$: 209.4(3) pm, $n = 2$: 210.2(5) pm). The increase of $Xe-F_b$ is partially in a accordance with decrease of $Xe-F_t$ bond lengths ($n = 6$: 193.4(4) pm, $n = 4$: 193.9(4) pm, $n = 2$: 190.6(5) pm). All XeF_2 molecules in $[Cu(XeF_2)_n](SbF_6)_2$ compounds demonstrate rather strong asymmetry. Such a large difference between $Xe-F_t$ and $Xe-F_b$ bond lengths has also been found in $[Nd(XeF_2)_{2.5}](AsF_6)_3$ ($Xe-F_t$: 193.6 pm/191.8 pm, $Xe-F_b$: 207.9 pm/207.3 pm).[22] The $Xe-F_b$ bonds in $Cu(XeF_2)_2](SbF_6)_2$ are the longest (and consequently the corresponding $Xe-F_t$ distances are the shortest) among all $Xe-F_b$ bonds found in the known $[M^{x+}(XeF_2)_n](A)_x$ (M = Mg−Ba, Zn, Cd, Pb, La, Nd, A = BF_4, PF_6, etc.) complexes.[23] The large XeF_2 distortion is in accordance with the much higher electron affinity of Cu^{2+} (20.29 eV)[24] when compared with those of other M^{x+} cations in known $[M^{x+}(XeF_2)_x](A)_x$ compounds.[23] The higher electron affinity of M^{x+}, the stronger the interaction of the cation with the fluoride ions, resulting in a higher degree of covalency in the Cu−F(Xe) bond.

As in the case of $[Mg(XeF_2)_n](AsF_6)_2$ ($n = 4, 2$),[2] the XeF_2 molecules in $[Cu(XeF_2)_n](SbF_6)_2$ also have slightly distorted F−Xe−F angles ($n = 6$: 179.33°, $n = 4$: 177°, $n = 2$: 178.3°) because of the large number of long-range Xe•••F interactions ($n = 6$: 318−357 pm, $n = 4$: 316−359 pm, $n = 2$: 314−352 pm), which are below the sum of van der Waals radii of xenon and fluorine (363 pm).[25]

The Xe−F−Cu angles in $[Cu(XeF_2)_n](SbF_6)_2$ ($n = 6, 4$) have similar values (125° and 128°, respectively), whereas in $[Cu(XeF_2)_2](SbF_6)_2$ this angle is more open (170°). The variation in these angles is related to packing requirements.

Raman Spectra. Raman spectra obtained for the powdered samples resulting from eq 1 and Raman spectra obtained for single crystals of $[Cu(XeF_2)_2](SbF_6)_2$ were identical. Raman spectra of $[Cu(XeF_2)_2](SbF_6)_2$ are shown in Figure 6, and frequencies and assignements are given in Table 4. Raman spectra of pure $[Cu(XeF_2)_4](SbF_6)_2$ (Table 4, Figure 7) were recorded on single crystals only because powdered material was always contaminated with small amounts of $Xe_2F_3SbF_6$. The Raman spectra of $[Cu(XeF_2)_n](SbF_6)_2$ and $Xe_2F_3SbF_6$ have very similar features, that is, the strongest split band is almost at the same position. The Raman spectra of $[Cu(XeF_2)_2](SbF_6)_2$ and $Xe_2F_3SbF_6$ are clearly distinguishable only in the 100−200 cm^{-1} region. These similaritites made it difficult to indentify new phases in the $Cu(SbF_6)_2/XeF_2$ system, when the Raman spectra of the single crystals are not available.

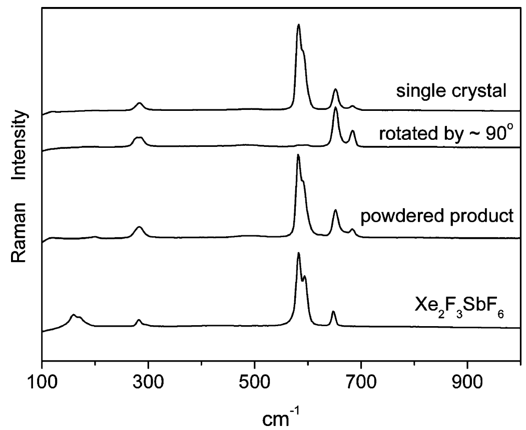

Figure 6. Raman spectra of $[Cu(XeF_2)_2](SbF_6)_2$ (recorded on a single crystal at different orientations), Raman spectrum of the powdered product of reaction between $Cu(SbF_6)_2$ and $2XeF_2$, and Raman spectrum of $Xe_2F_3SbF_6$.

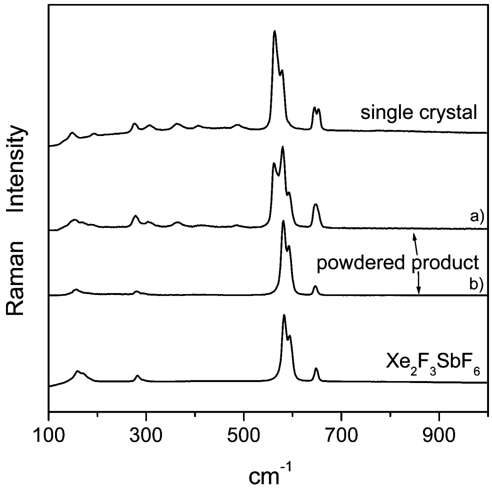

Figure 7. Raman spectrum of $[Cu(XeF_2)_4](SbF_6)_2$ (recorded on a single crystal), Raman spectra of the powdered product of reaction between $Cu(SbF_6)_2$ and $4XeF_2$ recorded on different spots of the same sample [(a) mixture of $[Cu(XeF_2)_2](SbF_6)_2$ and $Xe_2F_3SbF_6$, (b) $Xe_2F_3SbF_6$ only], and the Raman spectrum of pure $Xe_2F_3SbF_6$.

On the basis of the previous studies,[17,26] the most intense split bands occurring at 562/578 cm^{-1} ($[Cu(XeF_2)_4](SbF_6)_2$) and 582/591 cm^{-1} ($[Cu(XeF_2)_2](SbF_6)_2$) were readily assigned to $Xe-F_t$ vibrations between xenon and the terminal fluorine atom (F_t). Splitting is a consequence of weak vibra-

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tional coupling of XeF_2 molecules within the unit cell. The $Xe-F_t$ bond-stretching frequencies for $[Cu(XeF_2)_2](SbF_6)_2$ are the highest observed so far and are in agreement with the shortest $Xe-F_t$ bond distances found among the known $[M(XeF_2)_n](XF_6)$ complexes.

It is interesting to note, that the split band (578/$\sim$590 cm^{-1}) is also clearly visible in the Raman spectrum of $[Mg(XeF_2)_2](AsF_6)_2$, although in the accompanying discussion this splitting has not been mentioned.[2]

The reported $Xe-F_b$ bridging stretching frequencies occur in the 412−479 cm^{-1} region[2,22,27] and the XeF_2 bends are usually below 200 cm^{-1}.[28] Because the band at 486 cm^{-1} in Raman spectrum of $[Cu(XeF_2)_4](SbF_6)_2$ appears to be too high for such a long $Xe-F_b$ bond, the very weak band at 407 cm^{-1} is assigned to this vibration instead. The bands in the 148−200 cm^{-1} region of the spectrum could be assigned to $\delta(XeF_2)$ modes, although some of the peaks may belong to $\delta(SbFCu)$ modes.

Two bands at 280/284 cm^{-1} and a band at 652 cm^{-1} in the Raman spectrum of $[Cu(XeF_2)_2](SbF_6)_2$ can be assigned to bending (υ_5) and symmetric stretching (υ_1) modes of the $[SbF_6]^-$ anion, respectively. As in $XeFSbF_6$,[29] the band at 684 cm^{-1} may be assigned to the formally inactive $\upsilon_3(SbF_6)$ mode, which appears because of the site symmetry lowering. The $\upsilon_2(SbF_6)$ mode is probably small and hidden under $\upsilon(Xe-F_t)$ peaks.

For $[Cu(XeF_2)_4](SbF_6)_2$, the situation is more complicated because it contains two crystallographic distinguishable $[SbF_6]^-$ anions where additional coupling is possible. One of the $[SbF_6]^-$ units bridges two copper atoms and the other one is free. The medium weak bands at 644 and 655 cm^{-1} are attributed to symmetric stretchs (υ_1) of isolated and bridging $[SbF_6]^-$ anions, respectively. The band at 277 cm^{-1} corresponds to the υ_5 mode. The assignments of the remaining peaks at 307, 364, and 486 cm^{-1} are problematic. The vibrational band at 364 cm^{-1} appears to be too high for the $\upsilon_4(SbF_6)$ mode[29] but is in the range expected for the $M\cdots FSb$ stretch[30,31] and could also be assigned to the $Cu\cdots FSb$ stretch. The weak band at 486 cm^{-1} is in the region typical for $Sb-F_b$ stretching modes.[31,32] The remaining band at 307 cm^{-1} could be tentatively assigned to the formally Raman inactive $\upsilon_4(SbF_6)$ mode because of the solid-state effects.

Conclusions

Two new compounds containing XeF_2 ligands bound to Cu^{2+} were prepared and characterized. Together with $[Cu(XeF_2)_6](SbF_6)_2$, they complete the series in the $Cu(SbF_6)_2/XeF_2$ system. Raman spectra recorded on single crystals were found to be a very powerful tool for identification and for checking the purity of the isolated products of the $Cu(SbF_6)_2/XeF_2$ system. On the basis of the Raman spectra, it was found that previously reported[1] reaction between $CuSbF_6$ (1.1 mmol) and XeF_2 (3 mmol), and the reaction between CuF_2 and $Xe_2F_3SbF_6$ in molar ratio 1:2, initially yielded a $[Cu(XeF_2)_4](SbF_6)_2/Xe_2F_3SbF_6/CuF_2$ and not a $[Cu(XeF_2)_6](SbF_6)_2/Xe_2F_3SbF_6/CuF_2$ mixture. The XeF_2 which had been added to the former mixture prior to crystallization, allowed the growth of several single crystals of $[Cu(XeF_2)_6](SbF_6)_2$.

The proposed value for the Xe−F distance in the $[XeF]^+$ cation is less than 190 pm[33,34] with a stretching frequency greater than 600 cm^{-1}.[35] Although XeF_2 in $[Cu(XeF_2)_2](SbF_6)_2$ is still far from being $[XeF]^+F^-$, coordinated XeF_2 $[d(Xe-F_t) = 190.6(5)$ pm and $\upsilon(Xe-F_t) = 582/591\ cm^{-1}$; $d(Xe\cdots F_b) = 210.2(5)$ pm] has the highest $[F-Xe]^+\cdots F^-$ character among all known $[M^{x+}(XeF_2)_n](A)_x$ (M = metal cation, A = BF_4, PF_6, AsF_6, SbF_6, BiF_6) complexes. A consequence of this are the high covalencies of the Cu−F(Xe) bonds and stronger attraction of XeF_2 by the metal cation.

Acknowledgment. The authors gratefully acknowledge the Slovenian Research Agency (ARRS) for financial support of the present study within the research program: P1-0045 Inorganic Chemistry and Technology. We are also grateful to Dr. Maja Ponikvar for the chemical analyses.

Supporting Information Available: X-ray crystallographic files in CIF format for $[Cu(XeF_2)_4](SbF_6)_2$ and $[Cu(XeF_2)_2](SbF_6)_2$.This material is available free of charge via the Internet at http://pubs.acs.org.

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