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Communications

Preparations, X-ray Crystal Structures, and FT-Raman Spectra of $M_3Cl_3AsF_6$ (M = S, Se) Containing the Novel Sulfur–Chlorine and Selenium–Chlorine Cations $ClS^+(Cl)SSCl$ and $ClSe^+(Cl)SeSeCl$

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During the past decade we have discovered the rich chemistry of the sulfur/selenium iodine and sulfur/selenium bromine cations, examples of which include S_7I^+, $(S_7I)_2I^{3+}$, $M_2I_4^{2+}$,[1] $(Se_6I^+)_n$, $Se_6I_2^{2+}$, S_7Br^+, $Se_2Br_5^+$, and $M_3Br_3^+$ [2] (M = S, Se).[3] These cations maximize positive charge delocalization giving rise to thermodynamically stable π bonds and have in many cases cluster-like geometries.[3] In contrast, except for MCl_3^+ (M = S, Se),[4,5] the only example of a sulfur/selenium chlorine cation to be unambiguously characterized is Se_9Cl^+,[6] although Raman evidence has been presented for the unstable S_7Cl^+ cation.[7] In addition, $S_2Cl_3^+$ and $Se_2Cl_3^+$ have been claimed in solution[8a] and SCl^+ has been claimed in the solid state.[8b] The evidence suggested that lower sulfur and selenium/chlorine cations were less stable than their bromo and iodo analogues and might only exist as reactive intermediates. However, we have succeeded in preparing $S_3Cl_3AsF_6$ and $Se_3Cl_3AsF_6$, containing the first example of $M_3Cl_3^+$ cations, by the reaction of MCl_3AsF_6 and M (M = S, Se) using sulfur dioxide as solvent. The syntheses and the characterizations of these cations are the subject of this brief communication.

The salt $Se_3Cl_3AsF_6$ was prepared according to eq 1 by the reaction of $SeCl_3AsF_6$ (0.466 g, 1.24 mmol) and selenium (0.197 g, 2.44 mmol) in liquid sulfur dioxide, SO_2 (5.67 g), in a two-bulb glass vessel.[9] After 6 h of stirring at room temperature, addition of sulfuryl chloride fluoride, SO_2ClF (0.8 g), and slow removal of the solvent into the second bulb (ΔT = 4 °C) produced large crystals (red and black in transmitted and reflected light, respectively) of $Se_3Cl_3AsF_6$ (0.652 g, 1.23 mmol, yield 99% based on $SeCl_3AsF_6$). $S_3Cl_3AsF_6$ (1.304 g, 3.33 mmol) was similarly quantitatively prepared from SCl_3AsF_6 (1.106 g, 3.38 mmol) and sulfur (0.217 g, 0.85 mmol) in sulfur dioxide solution (5.11 g). Crystals of $S_3Cl_3AsF_6$ are brownish yellow and brown in transmitted and reflected light, respectively. The salts M_3Cl_3-

$$SeCl_3AsF_6 + 2Se \xrightarrow{SO_2} Se_3Cl_3AsF_6 \tag{1}$$

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(10) **$Se_3Cl_3AsF_6$:** M = 532.15, monoclinic, space group $P2_1/c$, a = 12.162(1) Å, b = 7.8457(9) Å, c = 12.108(1) Å, β = 105.052(7)°, V = 1115.7(2) Å^3, Z = 4, D_c = 3.187 g cm^{-1}, μ(Mo Kα) = 13.57 mm^{-1}, λ(Mo Kα) = 0.710 69 Å, $F(000)$ = 960.79, crystal size 0.36 × 0.24 × 0.16 mm^3. Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation using ω–2θ scans ($2\theta_{max}$ of 50.0°), resulting in 1945 unique reflections, 1458 of which were considered observed [$I \geq 0.5\sigma(I)$]. The data were corrected for Lorentz and polarization effects. Due to the orientation of the crystal upon mounting, suitable reflections for ψ scans could not be found, despite extensive searching. Consequently, an absorption correction was not performed. In addition, the anisotropic displacement ellipsoids do not show any pronounced parallel anisotropies often found in structures where absorption presents a serious systematic error. The structure was refined by full-matrix least-squares procedures to residuals of R = 0.083 and R_w = 0.084 for 1458 observed reflections and 119 parameters. All atoms were assigned anisotropic displacement parameters. Calculations were performed using the PC implementation of the NRCVAX program package.[11] **$S_3Cl_3AsF_6$:** M = 391.45, triclinic, space group $P\bar{1}$, a = 8.026(5) Å, b = 10.023(5) Å, c = 7.609(5) Å, α = 111.70(4)°, β = 115.87(5)°, γ = 82.36(5)°, V = 511(1) Å^3, Z = 2, D_c = 2.547 g cm^{-3}, μ(Mo Kα) = 47.42 mm^{-1}, λ(Mo Kα) = 0.710 69 Å, $F(000)$ = 372, crystal size 0.23 × 0.25 × 0.20 mm^3. Data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation at a temperature of −60 ± 1 °C using ω–2θ scans ($2\theta_{max}$ of 46.1°). Of the 1347 reflections collected, 1226 were unique (R_{int} = 0.062). The structure was determined by direct methods (SHELXS 86),[12] and the data were corrected for Lorentz and polarization effects and for absorption using the program DIFABS.[13] Refinement by full-matrix least-squares procedures with all atoms assigned anisotropic thermal parameters resulted in the final residuals R = 0.0590 and R_w = 0.0590 for 929 observed reflections [$I \geq 3\sigma(I)$] and 118 parameters. The bridging atoms in the two disordered rings were refined as sulfur in one ring and as chlorine in the other. The bridging atoms are labeled as S/Cl in Figure 2. All calculations were performed using the program SHELX 76.[14] Scattering factors for both structure determinations were taken from ref 15, and effects of anomalous dispersion were included in F_c using the values of Cromer.[16]

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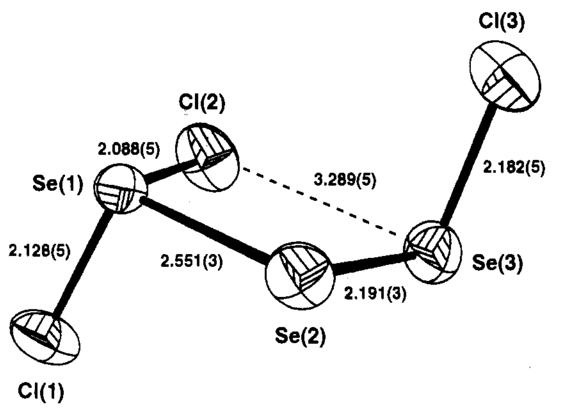


Figure 1. Structure of the ClSe$^+$(Cl)SeSeCl cation. Bond distances (Å) are given in the figure. Angles (deg): Cl(2)–Se(1)–Cl(1) 99.77(22), Cl(1)–Se(1)–Se(2) 99.97(15), Cl(2)–Se(1)–Se(2) 96.84(16), Se(1)–Se(2)–Se(3) 102.87(9), Se(2)–Se(3)–Cl(3) 104.41(18), Cl(1)–Se(1)–Se(2)–Se(3) 102.4(2), Cl(2)–Se(1)–Se(2)–Se(3) 1.2(1), Se(1)–Se(2)–Se(3)–Cl(3) 87.0(2). Shortest intercationic contact (<3.8 Å): Se(3)···Cl(3) 3.497(6) Å. Shortest cation–anion contacts (<3.0 Å): Se(1)···F(2) 2.688(13), Se(1)···F(4) 2.804(14) Å.

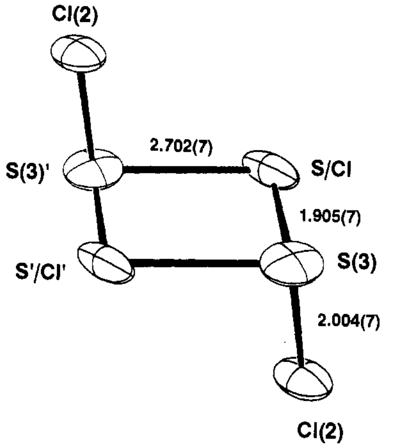
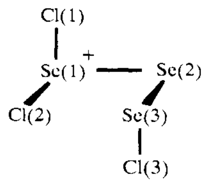


Figure 2. Structure of one of the two crystallographically different disordered ClS$^+$(Cl)(S/Cl)SCl cations. Bond distances (Å) are given in the figure. Angles (deg): Cl(2)–S(3)–S/Cl 106.3(3), Cl(2)–S(3)–S′/Cl′ 97.3(3), S/Cl–S(3)–S/Cl′ 88.0(3), S(3)–S/Cl–S(3)′ 92.0(3). The second disordered cation has similar bond distances and angles, and the data are deposited as supplementary material.

AsF_6 (M = S, Se) are stored without decomposition at −20 °C for 4 months but are less stable than their bromo analogues.

The crystal structures of the $M_3Cl_3AsF_6$ salts consist of $M_3Cl_3^+$ cations and AsF_6^- anions (M = S, Se). The structure of the ClSe$^+$(Cl)SeSeCl cation,[10] shown in Figure 1, is very similar to that of the BrSe$^+$(Br)SeSeBr cation in $Se_3Br_3AsF_6$.[2] Both adopt structures containing an intercationic chalcogen–halogen contact [Cl(2)···Se(3) = 3.289(5) Å; torsion angle Cl(2)Se(1)Se(2)Se(3) = 1.2(1)°] and substantial selenium–selenium bond alternation (see Figure 2) (bond orders: Se(1)–Se(2) 0.4, Se(2)–Se(3) 1.7[17]) arising from positive charge delocalization with valence bond structure 2, in addition to 1, making a substantial contribution to the overall structure and leading to substantial 4pπ–4pπ bonding between Se(2) and Se(3). Such charge delocalization would not be possible in $M_2Cl_3^+$ (M = S, Se), and consistently attempts to prepare $M_2Cl_3AsF_6$ by the same route lead to mixtures of MCl_3AsF_6 and $M_3Cl_3AsF_6$ (FT-Raman spectra). The Se(2)–Se(3) bond distance of 2.191(3) Å and Se(1)–Cl(2) bond distance of 2.088(5) Å appear to be the shortest bond distances of their class so far reported in isolated compounds. The Se$^+$–Cl bonds [Se(1)–Cl(1) = 2.128(5) Å and Se(1)–Cl(2) = 2.088(5) Å] are significantly shorter (and stronger) than Se(3)–Cl(3) [2.182(5) Å], containing the neutral two-coordinate selenium. The bond shortening in Se$^+$–Cl is a result of 3pπ → 4pπ back-bonding, accompanied by positive charge delocalization.



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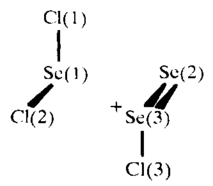

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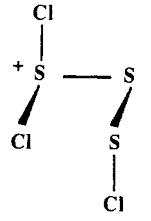
The X-ray structure of ClS$^+$(Cl)SSCl(AsF_6)[10] (Figure 2) contains two crystallographically different disordered $S_3Cl_3^+$ cations. The disorder arises from the superimposition of two ordered cations 3 and 4, each with a structure similar to that of the selenium analogue. Thus the X-ray results are consistent with the presence of the ClS$^+$(Cl)SSCl cation. The FT-Raman spectra of both cations (Table 1)) show peaks attributable to the stretching vibrations of the strong and weak M–M bonds, M^+Cl_2 stretches (similar to those in MCl_3AsF_6), and another M–Cl stretch at lower frequency corresponding to the vibration of the neutral M–Cl bond (similar to that in M_2Cl_2), providing further evidence for the similarity of the two $M_3Cl_3^+$ cations. Since reliable S–S bond distances could not be obtained for $S_3Cl_3^+$, they were estimated from a plot of known S–S stretching frequencies versus S–S bond distances, which yielded the linear relationship $\nu_{SS} = (3124.16 - 1294.51 d_{SS})$.[21] The S(2)–S(3) and S(1)–S(2) (for numbering of the atoms see Figure 1) stretching frequencies at 614 and 223 cm^{-1} correspond to bond distances of



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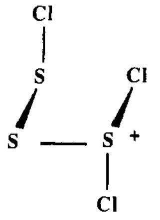

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(17) Bond orders were estimated using a variation of Pauling's[18] bond distance–bond order relationship, $D(n') = D_1 - b \log n'$, where n' is the bond order, $D(n')$ is the observed bond length, D_1 is the single-bond distance, and b is a constant. Selenium–selenium bond orders were estimated using the relationship $D(n') = 2.336 - 0.611 \log n'$, where 2.336 Å is the observed Se–Se single-bond distance in Se_8.[19] The constant 0.611 was determined by assuming that the bond order in Se_2(g) (bond distance = 2.152(3) Å)[20] is 2. Sulfur–sulfur bond orders were estimated using the relationship $D(n') = 2.048 - 0.526 \log n'$ (see ref 1) and the S–S single-bond distance observed in S_8 (2.048 Å).

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(21) The linear relationship was derived by extrapolation using S–S stretching frequencies and bond distances found for compounds containing ordinary σ-SS or (σ+π)-SS bonds; compounds containing (π*–π*)-SS bonds (e.g. in S_4N_4) were excluded (for a discussion of (π*–π*) bonds see: Burford, N.; Passmore, J.; Sanders, J. C. P. From Atoms to Polymers. Isoelectronic Analogies. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds., Verlag Chemie: Deerfield Beach, FL, 1989; p 53 and references therein). Complete details will be given in the full paper.

Table 1. Vibrational Frequencies (cm^{-1}) Attributable to Cl_2M^+MMCl (M = S, Se) in the FT-Raman Spectra of $M_3Cl_3AsF_6$[a–c]

Cl_2S^+SSCl	$Cl_2Se^+SeSeCl$	assignment
614 (7, br)		$\nu\{S(2)S(3)\}$
556 (6, br)	440 (30)	$\nu_{as}\{Cl_2S(1)\}/\nu_{as}\{Cl_2Se(1)\}$
522 (4, br)	418 (6)	$\nu_s\{Cl_2S(1)\}/\nu_s\{Cl_2Se(1)\}$
468 (7, br)	365 (20)	$\nu\{S(3)Cl\}/\nu\{Se(3)Cl\}$
	323 (15)	$\nu\{Se(2)Se(3)\}$
275 (10)	189 (20)	$\delta_s\{ClS(1)S(2)\}/\delta_s\{ClSe(1)Se(2)\}$
223 (100)[d]	170 (100)	$\nu\{S(1)S(2)\}/\nu\{Se(1)Se(2)\}$
256 (30)	151 (30)	$\delta_{as}\{ClS(1)S(2)\}/\delta_{as}\{ClSe(1)Se(2)\}$
170 (2)	124 (10)	$\delta\{S(2)S(3)Cl\}/\delta\{Se(2)Se(3)Cl\}$
135 (70)	109 (30)	$\delta\{S(1)S(2)S(3)\}/\delta\{Se(1)Se(2)Se(3)\}$
		$\delta\{Cl_2S(1)\}/\delta\{Cl_2Se(1)\}$
		$S_3Cl_3^+$ torsion
	93 (5)	$Se_3Cl_3^+$ torsion

[a] FT-Raman spectra were measured on a FT-IR spectrometer (Bruker IFS66) equipped with a FT-Raman accessory (Bruker FRA106) using a Nd–YAG laser (emission wavelength 1064 nm). The data were collected in the backscattering mode (180° excitation; resolution 4 cm^{-1}). The FT-Raman spectra of $S_3Cl_3AsF_6$ and $Se_3Cl_3AsF_6$ were obtained at ca. 100 K with laser powers of 19 and 34 mW, respectively (300 scans). Relative intensities (peak heights) are given in parentheses. [b] The frequencies for the AsF_6^- counterion of the $S_3Cl_3^+$ salt are 679 (10), 577 (1), 368 (3) and for the $Se_3Cl_3^+$ salt are 682 (20), 663 (2), 584 (2), 558 (6), [398 (6), 389 (6)], 376 (6) cm^{-1}. [c] See the structure of $Cl_2Se^+SeSeCl$ in Figure 1 for labeling of the chalcogen atoms. [d] The intensities of SS stretching bands increase with increasing SS bond distance,[26] and we have found this is also the case for selenium.[27]

1.94 and 2.24 Å, respectively. The corresponding bond orders are 1.6 and 0.4, respectively (see ref 17). The S–Cl bond distances were similarly estimated to be 1.98 Å (r_{av} in the $Cl_2S(1)^+$ fragment) and 2.06 Å (SS–Cl fragment) from the SCl stretching frequencies at 557, 522 cm^{-1} $\{Cl_2S(1)\}$ and at 468 cm^{-1} $\{S(3)Cl\}$ by comparison with related sulfur/chlorine compounds [$\nu_{SCl} = (1868.13 - 674.20 d_{SCl})$]. The structural parameters for the $ClS^+(Cl)SSCl$ cation estimated from the vibrational data are supported by *ab initio* calculations (STO-3G* level)[22] and are in agreement with the crystal data.

The preparation of $M_3Cl_3^+$ is formally an insertion of chalcogen atoms into the M–Cl bond in MCl_3^+ and is to our knowledge only known for neutral species (cf. formation of S_xCl_2 from sulfur and S_2Cl_2).[23] This reaction type may provide access to a family of related chalcogen–halogen salts, and the isolation of $M_3Cl_3AsF_6$ implies that other chlorosulfur and chloroselenium cations may be isolatable. In addition, we note the utility of FT-Raman spectroscopy for the characterization of highly colored reaction products.[24]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (T.S.C., and J.P.) and the donors of the Petroleum Research Fund (J.P.), administered by the American Chemical Society, for support of this research.

Supplementary Material Available: Text and tables giving details of the crystallographic data collection and listings of crystal data, positional and isotropic thermal parameters, anisotropic thermal parameters, bond distances and angles, and torsional angles for $S_3Cl_3AsF_6$ and $Se_3Cl_3AsF_6$ and ORTEP diagrams of the two crystallographically different disordered $ClS^+(Cl)(S/Cl)SCl$ cations (15 pages). Ordering information is given on any current masthead page.

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(22) STO-3G*-optimized parameters (GAUSSIAN 92):[22a] *R*[S(1)–S(2)] = 2.234 Å, *R*[S(2)–S(3)] = 1.884 Å, *R*[S(1)–Cl(2)] = 1.961 Å, *R*[S(1)–Cl(1)] = 1.971 Å, *R*[S(3)–Cl(3)] = 1.988 Å (for numbering of the atoms see Figure 1). (a) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision E.1; Gaussian, Inc.: Pittsburgh, PA, 1992.

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(24) The developments in the area of FT-Raman spectroscopy (using a Nd–YAG laser instead of an argon laser) allow us to use this technique to successfully characterize colored products (e.g.: $Ph\overline{CNSSN}^{\bullet}$, $p\text{-}O_2NC_6H_4\overline{CNSNS}^{\bullet}$, black;[25] I_2, I_3AsF_6, I_5AsF_6, $S_2I_4AsF_6$, black; unpublished results).

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