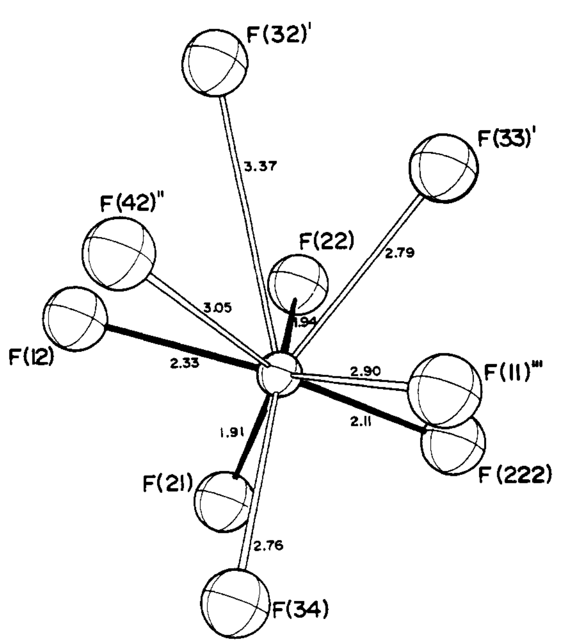

Figure 6. View of the Sb(III) atom of the $Sb_4F_{17}^-$ anion directed toward the assumed direction of the lone pair of electrons of Sb(III). Interionic contacts are indicated by unfilled bonds.

is 180° and the lone pairs on the two Sb(III) atoms are staggered. The Sb(III)–F–Sb(III) bond angles in previously observed $Sb_2F_5^+$ units range from 149.8° in $(SbF_3)_3SbF_5$[23] to 180° in $(SbF_3)_6(SbF_5)_5$.[24] The analogous angle in the isoelectronic $Sn_2F_5^-$ anion[25] is 134°. The primary geometry of the Sb(III) atom in the $Sb_4F_{17}^-$ anion can be described as trigonal-bipyramidal AX_4E, where the lone pair of electrons and the two terminal fluorine atoms occupy the equatorial plane and the bridging fluorine atoms are axial (see Sb(2), Figure 5). In the present structure there are five additional Sb(III)···F contacts shorter than the sum of the van der Waals radii of Sb and F, and overall the environment may be described as $AX_4YY'_4E$[26] (Figure 6). This is a distorted version of an $AX_3Y_3Y'_3E$ arrangement based on a tricapped trigonal prism with (F(222), F(21), F(22)), (F(12), F(34), F(33)'), and (F(32)', F(11)''', F(42)'') as the X, Y, and Y' atoms.[26] A bond valence calculation[27] using all interactions around Sb(III) gives a sum of 3.12. The crystal packing consists of layers of $Sb_4F_{17}^-$ and SbF_6^- anions approximately perpendicular to *b* linked by the Sb(III)···F interactions involving the remaining SbF_6^- anions. The cations are situated in stacks between these anions.

Conclusions

The first examples of mixed S/Se polyatomic cations, $S_xSe_{4-x}^{2+}$, have been prepared by direct oxidation of the elements with AsF_5 and by scrambling of S_4^{2+} and Se_4^{2+} cations in SO_2 solution. The square-planar geometry of the $S_xSe_{4-x}^{2+}$ cations and the existence of the $Sb_4F_{17}^-$ anion have been established by the crystal structure of the new compound $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$. Evidence for a second series of S/Se cations has been obtained by ^{77}Se NMR spectroscopy. The chemical shifts of these species indicate that they are not isostructural with the presently known polyatomic cations of selenium.

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Registry No. $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$, 101248-77-5; $(Se_4)(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$, 82434-40-0; $(S_{3.0}Se_{1.0})(AsF_6)_2$, 101248-72-0; Se_4, 12310-32-6; Se_3S, 101248-73-1; *cis*-Se_2S_2, 101248-74-2; *trans*-Se_2S_2, 101248-75-3; SeS_3, 101248-71-9; Se, 7782-49-2; S, 7704-34-9; ^{77}Se, 14681-72-2.

Supplementary Material Available: Supplementary Tables I–III, containing complete bond lengths and bond angles, anisotropic thermal parameters, and final structure factor amplitudes for $(S_{3.0}Se_{1.0})_2(Sb_4F_{17})(SbF_6)_3$, respectively (21 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1, and Lash-Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Preparation and Structure of $[W_2(CO)_{10}Se_4][AsF_6]_2$ and Related Compounds

M. J. Collins,[†] R. J. Gillespie,*[†] J. W. Kolis,[†] and J. F. Sawyer[‡]

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The reactions of $Se_4(AsF_6)_2$, $Se_8(AsF_6)_2$, and $Se_{10}(SbF_6)_2$ with $Mo(CO)_6$ and $W(CO)_6$ in liquid SO_2 give the diamagnetic products $[M_2(CO)_{10}Se_4][EF_6]_2$ (M = Mo, W; E = As, Sb) in high yields. The structure of $[W_2(CO)_{10}Se_4][AsF_6]_2$ (Ia) has been established by X-ray crystallography. Crystals of Ia are monoclinic, space group $P2_1/c$, with a = 8.688 (1) Å, b = 7.036 (1) Å, c = 21.767 (1) Å, β = 95.30 (1)°, U = 1324.9 (4) Å^3, and D_{calcd} = 3.36 g cm^{-3} for Z = 2. The structure consists of two centrosymmetrically related pentagonal-bipyramidal $W(CO)_5(\eta^2\text{-}Se_2)^+$ groups linked by weak Se–Se bonds of length 3.015 (2) Å between the diselenide groups. The Se–Se distance in the η^2-Se_2 moiety (2.213 (2) Å) is the shortest solid-state Se–Se bond reported to date. The interactions between the diselenide groups are analogous to those observed in the $Se_4S_2N_4^{2+}$ cation, and the bonding is discussed with use of this cation as a model.

Introduction

The chalcogen cations such as Se_4^{2+}, Te_6^{4+}, S_8^{2+}, and S_{19}^{2+} are now well-known, and a considerable amount of structural and spectroscopic information has been obtained in recent years,[1,2] but their chemistry has not been extensively investigated. Reactions of these cations with elemental sulfur, selenium, and tellurium yield a variety of heteroatomic clusters.[3] The cations react with perfluorocarbons, giving various perfluorinated tellurides, selenides, and sulfides.[4] Reaction with hydrocarbons results

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* To whom correspondence should be addressed.
[†] McMaster University.
[‡] University of Toronto.

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in reduction of the cations and production of sulfides and selenides.[5] Se_4^{2+} and S_8^{2+} react with S_4N_4 to form $[Se_4S_2N_4]^{2+}$ and $[S_6N_4]^{2+}$, respectively.[6,7] In addition, sulfur and selenium cations react with halogens and halides to produce heteroatomic cations.[8]

Because the square S_4^{2+}, Se_4^{2+}, and Te_4^{2+} species have delocalized π orbitals containing six electrons,[9] we and others[10] have been investigating the possibility that these cations might react with transition-metal carbonyls to form six-π-electron-donor complexes. In this paper we report a study of the reactions of $Se_4(AsF_6)$,[2] $Se_8(AsF_6)_2$, and $Se_{10}(SbF_6)_2$ with $Mo(CO)_6$ and $W(CO)_6$, which give high yields of $[W_2(CO)_{10}Se_4][AsF_6]_2$ and $[Mo(CO)_{10}Se_4][SbF_6]_2$. These new compounds have been characterized by chemical analysis, IR spectroscopy, and X-ray crystallography. After this work was completed, a communication appeared describing the structure of $[W_2(CO)_{10}Se_4][SbF_6]_2$, which is in close agreement with our results.[10]

Experimental Section

Selenium powder (K-L Laboratories) was dried in vacuo overnight. Arsenic trifluoride was prepared by the method of Hoffman[11] and purified by vacuum distillation into an FEP tube containing dry NaF. Arsenic pentafluoride was prepared by fluorination of AsF_3. Antimony pentafluoride (Ozark Mahoning) was vacuum distilled in an all-glass apparatus and stored under nitrogen in an FEP bottle. Sulfur dioxide (Matheson) was stored over P_2O_5 for several days before use. $Mo(CO)_6$ and $W(CO)_6$ (Aldrich) were used as received. Because of the extreme moisture sensitivity of the reactants and products, all reactions were performed on a vacuum line and solids were manipulated in a glovebox containing dried nitrogen. Reactions were performed in flame-dried glass vessels consisting of two 100-mL round-bottom flasks, one containing a Teflon-coated magnetic stir bar, connected by a medium-porosity glass frit.[12] After the reactants and solvents had been added, the vessel was flame-sealed on a vacuum line. $Se_4(AsF_6)_2$, $Se_8(AsF_6)$, and $Se_{10}(SbF_6)_2$ were prepared by methods previously reported.[12,13] IR spectra were all obtained as Nujol mulls between AgCl plates or in sealed polyethylene bags on a Perkin-Elmer 283 spectrometer. Magnetic measurements were made by the Gouy method. Analyses for selenium and AsF_6^- were performed with use of standard literature methods.[14,15]

Synthesis of $[M_2(CO)_{10}Se_4][AsF_6]_2$ (M = Mo, W). In a typical preparation $W(CO)_6$ (0.250 g, 0.712 mmol) and $Se_4(AsF_6)_2$ (0.246 g, 0.355 mmol) were added to one flask of the reaction vessel. Sulfur dioxide (25 mL) was distilled into the flask and the apparatus sealed off. When the mixture was allowed to slowly warm to room temperature, the solution turned deep red as soon as the reactants started to dissolve. After 15 min of stirring, all the reactants had dissolved and a purple-black microcrystalline precipitate formed. After 1 h the reaction was complete and the pale green-brown solution was decanted from the product. The solid was washed with SO_2 and dried under vacuum; yield 0.413 g (86.7%). Anal. Calcd for $W_2C_{10}O_{10}Se_4As_2F_{12}$: Se, 23.54; AsF_6^-, 28.16. Found: Se, 23.10; AsF_6^-, 27.89. IR (Nujol): 2143 m, 2099 m, 2081 s, 2060 s, 2003 s, 690 sh, 562 m, 554 m, 534 m, 396 s, 327 m cm^{-1}. The molybdenum compound was prepared in a similar manner. Anal. Calcd for $Mo_2C_{10}O_{10}Se_4As_2F_{12}$: Se, 27.10; AsF_6^-, 32.41. Found: Se, 26.09; AsF_6^-, 31.34. IR (Nujol) 2140 m, 2102 m, 2088 s, 2075 s, 2010 s, 690 sh, 558 m, 550 m, 530 m, 394 s, 318 m cm^{-1}.

Table I. Crystal Data and Details of Intensity Measurements and Structure Refinement

compd	$[WSe_2(CO)_5]_2(AsF_6)_2$
system	monoclinic
a, Å	8.688 (1)
b, Å	7.036 (1)
c, Å	21.767 (1)
β, deg	95.30 (1)
U, Å^3	1324.9 (4)
fw	1341.4
Z	2 (dimers)
D_{calcd}, g cm^{-3}	3.36
μ(Mo K$\bar{\alpha}$), cm^{-1}	178.0
space group	$P2_1/c$
T, °C	23
reflecns used in cell determn	15
radiation	Mo K$\bar{\alpha}$ (λ = 0.71069 Å) graphite monochromator
diffractometer	Syntex $P2_1$
max 2θ, deg; scan type	55; θ–2θ
scan speeds, deg min^{-1} [a]	3.0–29.3
scan ranges,[b] deg	$(K\alpha_1 - 1.0)$–$(K\alpha_2 + 1.0)$
std reflecns (no./interval)	3/67
quadrants collected	$h,k,\pm l$
no. of data collected	3942 (inc stds)
abs corr cm (ABSORB, $10 \times 10 \times 5$ grid)	plate; {100}, 0.0068; {001}, 0.0034; (130) and $(1\bar{3}0)$, 0.0075 (A^* = 3.066–7.729)
structure soln	Patterson, least-squares, Fourier
no. of indep data	2791
no. of data with $F > 3\sigma(F)$	1998
R_1 for 6σ data	0.0403
R_2	0.0388
max shift/error, final cycle	0.15
wts	$\{\sigma^2(F) + 0.00053F^2\}^{-1}$
final diff Fourier, e Å^{-3}	0.60

[a] Dependent on intensity of a 2-s prescan. [b] Backgrounds measured by using stationary counter–stationary crystal on either side of the peak for a time equal to half the scan time for the peak.

Reaction of $M(CO)_6$ with $Se_8(AsF_6)_2$ (M = Mo, W). In a typical experiment $Mo(CO)_6$ (0.200 g, 0.758 mmol), $Se_8(AsF_6)_2$ (0.382 g, 0.379 mmol), and SO_2 (20 mL) were combined as above and the vessel was sealed off. When it was warmed to room temperature, the solution became intensely red. After 10 min black microcrystals precipitated and red selenium was observed on the walls of the flask. After 1 h the light brown-green solution was decanted and the dark solid, which was contaminated with some selenium, was isolated as before. Anal. Calcd for $Mo_2C_{10}O_{10}Se_4As_2F_{12}$: Se, 27.10; AsF_6^-, 32.41. Found: Se, 41.01; AsF_6^-, 26.12. IR (Nujol): 2140 m, 2102 m, 2086 s, 2072 s, 2010 s, 690 sh, 560 m, 550 m, 530 m, 394 s, 318 m cm^{-1}. IR (Nujol) for the tungsten compound: 2138 m, 2090 m sh, 2078 m sh, 2057 s, 2002 s, 690 sh, 558 m, 550 m, 530 m, 392 s, 325 m cm^{-1}.

Reaction of $Mo(CO)_6$ with $Se_{10}(SbF_6)_2$. This reaction was performed similarly to those previously described. $Mo(CO)_6$ (0.200 g, 0.758 mmol), $Se_{10}(SbF_6)_2$ (0.478, 0.380 mmol), and SO_2 (25 mL) were added to one flask of the reaction vessel, and the flask was allowed to warm to room temperature. After 1 h of stirring, black crystals were isolated as described above. Again, red selenium was visible on the walls of the flask. IR (Nujol): 2136 m, 2101 m, 2086 s, 2072 s, 2010 s, 965 m, 650 s, 560 m, 550 m, 530 m, 315 m, 278 s cm^{-1}.

Reaction of $Cr(CO)_6$ with $Se_4(AsF_6)_2$. $Cr(CO)_6$ (0.200 g, 0.869 mmol), $Se_4(AsF_6)_2$ (0.301 g, 0.430 mmol), and SO_2 (20 mL) were combined as above, and the reaction vessel was sealed. When the system was warmed to room temperature, an amorphous brick red powder precipitated. The infrared spectrum did not reveal the presence of any carbonyl groups or the AsF_6^- ion.

X-ray Crystallography. The product obtained from reactions in pure SO_2 was always microcrystalline. However, suitable single crystals of $[W_2(CO)_{10}Se_4][AsF_6]_2$ were obtained if mixed SO_2/AsF_3 (5:1 v/v) solvent was used. Black platelets were selected and sealed in Lindemann capillaries in a drybox equipped with a microscope. preliminary precession photographs were used to check crystal quality and to obtain space group and unit cell information. Further work on a Syntex $P2_1$ diffractometer gave the crystal data indicated in Table I. Details of the intensity measurements and structure refinement are also listed in Table I.

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Table II. Final Atomic Positional Parameters (×10^4) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
W(1)	2749.3 (6)	716.5 (7)	3842.7 (2)
Se(1)	4020.0 (16)	2332.9 (19)	4855.8 (6)
Se(2)	5674.4 (14)	1001.5 (21)	4271.8 (6)
As(1)	2036.4 (16)	1063.6 (21)	1346.4 (6)
F(1)	2409 (11)	1681 (14)	2105 (4)
F(2)	1821 (14)	3396 (15)	1147 (5)
F(3)	123 (10)	926 (19)	1446 (5)
F(4)	1689 (12)	436 (16)	584 (4)
F(5)	3947 (11)	1263 (16)	1236 (4)
F(6)	2253 (15)	−1260 (14)	1543 (5)
O(1)	3010 (13)	4744 (15)	3182 (5)
O(2)	−179 (12)	1769 (17)	4555 (5)
O(3)	−53 (15)	−5 (25)	2826 (5)
O(4)	2436 (12)	−3359 (14)	4441 (5)
O(5)	4398 (15)	−1332 (19)	2762 (5)
C(1)	2966 (16)	3320 (20)	3437 (7)
C(2)	844 (17)	1456 (21)	4303 (7)
C(3)	924 (20)	194 (24)	3169 (7)
C(4)	2601 (16)	−1886 (18)	4240 (6)
C(5)	3973 (17)	−626 (22)	3145 (6)

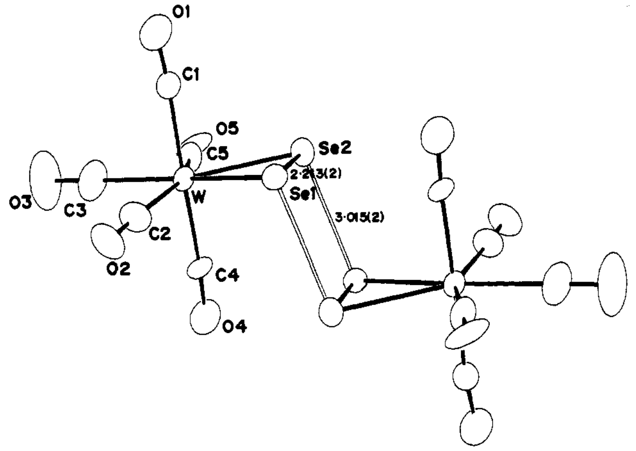

Figure 1. ORTEP drawing of the $[W_2(CO)_{10}Se_4]^{2+}$ dimer in the $[W_2(CO)_{10}Se_4][AsF_6]_2$ salt (Ia).

For the refinements, neutral-atom scattering factors in the analytical form were taken from standard sources.[16] Calculations were performed on CDC6400 and SEL 75 computers using programs in the XRAY 76[17] and SHELX[18] systems as well as local programs. The final atomic positional parameters and significant bond lengths, bond angles, and contact distances are given in Tables II and III.

Table III. Selected Bond Distances (Å), Bond Angles (deg), and Contact Distances (Å)^a

	Distances (Å)^b		
W(1)–Se(1)	2.632 (1)	As(1)–F(1)	1.710 (8)
–Se(2)	2.633 (1)	–F(2)	1.703 (10)
–C(1)	2.050 (14)	–F(3)	1.699 (9)
–C(2)	2.079 (15)	–F(4)	1.717 (9)
–C(3)	2.091 (15)	–F(5)	1.704 (9)
–C(4)	2.034 (13)	–F(6)	1.696 (10)
–C(5)	2.068 (15)	Se(1)···F(4)^{II}	3.110
Se(1)–Se(2)	2.213 (2)	···F(5)^{II}	3.168
Se(1)···Se(2)^{I}	3.015 (2)	···O(4)^{I}	3.387
C(1)–O(1)	1.15 (2)	···C(4)^{I}	3.394
C(2)–O(2)	1.11 (2)	Se(2)···Fe(2)^{III}	3.049
C(3)–O(3)	1.09 (2)	···F(6)^{IV}	3.270
C(4)–O(4)	1.14 (2)	···O(4)^{I}	3.528
C(5)–O(5)	1.14 (2)	···C(4)^{I}	3.497
	Angles (deg)		
Se(1)–W(1)–Se(2)	49.72 (4)	W(1)–C(1)–O(1)	175.6 (12)
–C(1)	85.8 (4)	W(1)–C(2)–O(2)	176.9 (14)
–C(2)	77.2 (4)	W(1)–C(3)–O(3)	176.9 (18)
–C(3)	153.6 (5)	W(1)–C(4)–O(4)	175.8 (12)
–C(4)	94.1 (3)	W(1)–C(5)–O(5)	178.3 (14)
–C(5)	129.4 (4)	F(1)–As(1)–F(2)	90.4 (5)
Se(2)–W(1)–C(1)	87.8 (4)	–F(3)	89.5 (5)
–C(2)	126.5 (4)	–F(4)	179.2 (5)
–C(2)	155.1 (5)	–F(5)	98.8 (4)
–C(4)	90.8 (4)	–F(6)	89.7 (5)
–C(5)	79.7 (4)	F(2)–As(1)–F(3)	90.1 (6)
C(1)–W(1)–C(2)	95.3 (6)	–F(4)	89.8 (5)
–C(3)	87.1 (6)	–F(5)	88.3 (5)
–C(4)	178.3 (5)	–F(6)	179.9 (4)
–C(5)	91.6 (6)	F(3)–As(1)–F(4)	91.2 (5)
C(2)–W(1)–C(3)	78.2 (6)	–F(5)	178.4 (6)
–C(4)	86.3 (6)	–F(6)	90.0 (6)
–C(5)	153.0 (6)	F(4)–As(1)–F(5)	88.4 (5)
C(3)–W(1)–C(4)	93.8 (5)	–F(6)	90.1 (5)
–C(5)	76.1 (6)	F(5)–As(1)–F(6)	91.6 (6)
C(4)–W(1)–C(5)	87.2 (5)		
W(1)–Se(1)–Se(2)	65.17 (5)		
–Se(2)′	101.37 (5)		
W(1)–Se(2)–Se(1)	65.11 (5)		
–Se(1)′	100.96 (5)		
Se(2)–Se(1)–Se(2)′	90.46		
Se(1)–Se(2)–Se(1)′	89.54		

^{a}Sum of van der Waals radii: Se + F, 3.35; Se + O, 3.40 Å. ^{b}Symmetry operations: (I) $1 - x, -y, 1 - z$; (II) $x, {}^1/_2 - y, {}^1/_2 + z$; (III) $1 - x, -{}^1/_2 + y, {}^1/_2 - z$; (IV) $1 - x, {}^1/_2 + y, {}^1/_2 - z$.

Table IV. Selenium–Selenium Distances in Side-Bonded η^2-Se_2 Complexes

compd	Se–Se dist, Å	ref
$CpMn(CO)_2(Se_2)$	2.263 (8)	24
$Os(CO)_2(PPh_3)_2(Se_2)$	2.321 (1)	19
$Fe_2(CO)_6(\mu\text{-}Se_2)$	2.293 (2)	20
$[Ir(dppe)_2Se_2]^+$	2.312 (3)	25
$Nb_2Cl_4(Se_2)_2(SMe_2)_4$	2.289 (3)	26
$[W_2(CO)_{10}Se_4][AsF_6]_2$	2.213 (2)	this work
$W_2Cl_8(\mu\text{-}Se)(\mu\text{-}Se_2)^{2-}$	2.255 (8)	21
$NbSe_2Cl_2$	2.272 (5)	28
$[(PtMe_3Br)_2Me_2Se_2]$	2.36 (1)	22
$[(Re(CO)_3Br)_2Ph_2Se_2]$	2.41 (2)	23
$Nb_2Cl_4Se_4(C_4H_8S)_4$	2.260 (5)	27
$[W_2(CO)_{10}Se_4][SbF_6]_2$	2.208 (1)	10

Results and Discussion

Structure of $[W_2(CO)_{10}Se_4][AsF_6]_2$ (Ia). The reaction of $Se_4(AsF_6)_2$ and $W(CO)_6$ gives $[W(CO)_5Se_2]_2[AsF_6]_2$, which has been characterized by X-ray crystallography. The geometry of the tungsten is pentagonal bipyramidal with three carbonyls and a diselenide group equatorial (see Figure 1). The equatorial atoms are planar to ±0.23 (2) Å (Table III) with C–W–C angles (76.1 and 78.2°) and C–W–Se angles (77.2 and 79.7°) distorted from the ideal value of 72° by the small Se–W–Se angle of 49.72 (4)°. Bond angles between the axial carbonyls and atoms in the equatorial plane are 85.8–95.3°. The diselenide group is tilted by 2.5° with respect to other atoms in the equatorial plane. An interesting feature of the molecule is that it is linked into dimers by long Se···Se bonds of length 3.015 (2) Å across the center of symmetry at (${}^1/_2$, 0, ${}^1/_2$) (Figure 1). The Se(1)–Se(2)–Se(2′)–Se(1′) plane makes an angle of 102.3° with the plane W(1)–Se(1)–Se(2) and 105.3° with the least-squares mean plane through all the equatorial atoms. This dimeric structure is very similar to that of the thiodiselenazyl cation $Se_4S_2N_4^{2+}$, in which pairs of $Se_2SN_2^+$ rings are linked by Se···Se interactions of lengths 3.121 (2) and 3.162 (2) Å (AsF_6^- salt) between the diselenide groups.[7] Diselenide units bridging one or two transition-metal atoms are known[19-28] (see Table IV), but in no case have analogous

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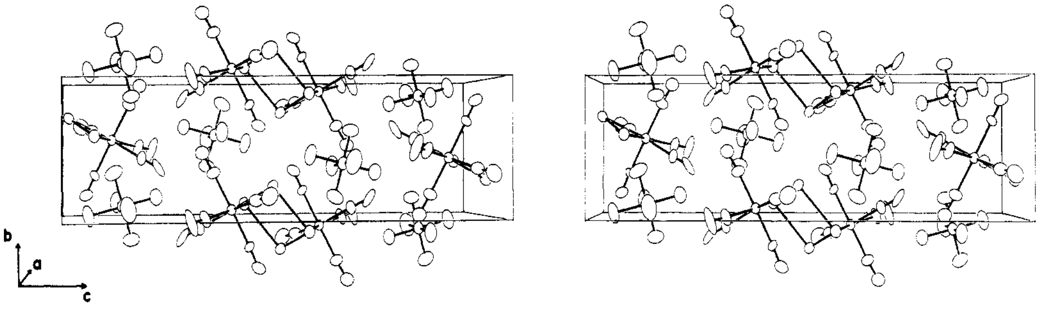

Figure 2. Stereoview of the unit cell of $[W_2(CO)_{10}Se_4][AsF_6]_2$ showing the well-separated anions and cations.

intermolecular Se···Se contacts been observed. In all these compounds the Se–Se distance is significantly shorter than the accepted single-bond distance (e.g. 2.335 Å in Se_8).[29]

In the present compound the Se–Se bond length is 2.213 (2) Å, which is even shorter than the bonds in Se_4^{2+} (2.286 (2) Å), which nominally have a bond order of 1.25.[9] The shortest distance previously reported in the solid state is in β-SeBr (2.241 Å).[30] Campana et al.[20] have drawn attention to the relationship between distance and bond order based on Pauling covalent radii. On the basis of their plot, an Se–Se distance of 2.21 Å implies a bond order of over 1.5. The Se–Se distance of 2.21 Å is very close to the value of 2.19 Å found for the gas species Se_2,[31] in which there is effectively a double bond.

The W–Se bond lengths of 2.632 (1) and 2.633 (1) Å in the present compound are significantly longer than W–Se distances in the $W_2Cl_8(Se_2)Se^{2-}$ anion. These are 2.558 (6) and 2.580 (6) Å to the bridging Se_2 group and 2.384 (7) and 2.409 (7) Å in the W–Se–W bridge.[21] A W=Se double-bond length of 2.225 (5) Å has been observed in $CH_3OCH_2CH_2OWCl_3Se$.[32]

The SbF_6^- salt of the compound has been prepared by a similar method recently and is essentially isostructural with this compound.[10] Its short Se–Se bond is even shorter than that in Ia (2.208 (1) Å), and the W–Se distances are similar to those in Ia but are slightly inequivalent (2.626 (1) and 2.631 (1) Å).

The η^2-Se_2^+ ligand in Ia appears to exert a significant trans influence. The CO bond trans to the Se_2 group (1.081 Å) is the shortest of the five CO bonds. The two axial CO groups have the longest bonds (1.153 and 1.142 Å) while the other equatorial CO bonds are intermediate in length. The trans CO also has the longest W–C bond (2.094 Å) while the axial CO's have the shortest W–C bonds (2.032 and 2.047 Å). This may imply that the Se_2^+ group is a reasonably good σ donor as well as a good π acceptor. This is in agreement with other workers who have proposed that η^2-S_2 and -Se_2 groups are better π acceptors than CO.[24]

The hexafluoroarsenate ion dimensions are normal with an average As–F bond length of 1.705 Å (Table III), and they are well separated from the cations (Figure 2).

Synthesis. The polyatomic selenium cations Se_4^{2+}, Se_8^{2+}, and Se_{10}^{2+} react with $Mo(CO)_6$ and $W(CO)_6$ in SO_2 to produce the cationic dimer I. The reaction is rapid and essentially quantitative.

$$2M(CO)_6 + [Se_{4+n}][EF_6]_2 \xrightarrow{SO_2} [M_2(CO)_{10}Se_4][EF_6]_2 + 2CO + nSe$$

Ia: M = W, E = As
Ib: M = Mo, E = As
Ic: M = W, E = Sb
Id: M = Mo, E = Sb

The mixture initially forms a deep red solution from which dark purple-black crystals precipitate. The red solution can be maintained at −78 °C overnight, but at room temperature the product forms quantitatively within 15 min. The four compounds are insoluble in SO_2 and CH_2Cl_2 and are decomposed by CH_3CN, CH_3NO_2, $(CH_3)_2CO$, and H_2SO_4. They are readily soluble in AsF_3 but appear to decompose after several hours. If $Se_4(AsF_6)_2$ is used as a reactant, an analytically pure crystalline sample can be obtained from the reaction mixture. When $Se_8(AsF_6)_2$ and $Se_{10}(SbF_6)_2$ are used, the same product is obtained but it is contaminated with elemental selenium. The reaction appears to take place via the initial formation of $M(CO)_5(SO_2)$. If the reaction is performed by first dissolving the metal carbonyl in SO_2, a yellow solution is formed with evolution of a gas, presumably CO. If this solution is added to the selenium cation, the reaction is almost instantaneous. The product I does not appear to react with an excess of metal carbonyl. However, it does react with an excess of Se_8^{2+}. If an SO_2 solution of $Se_8(AsF_6)_2$ is allowed to stand with solid I, the dark crystals slowly disappear and bright orange crystals form. This new product is stable indefinitely as long as it is in contact with an Se_8^{2+} solution. If the solution is removed, it decomposes in several hours to I, and Se_8^{2+}, which can be washed away with fresh SO_2. An IR spectrum of the orange product shows it to contain carbonyl and AsF_6^- groups.

Spectroscopy. The IR spectrum of $[W_2(CO)_{10}Se_4][AsF_6]_2$ is in full agreement with the crystal structure. The five bands between 2140 and 2000 cm^{-1} correspond to the CO groups on each metal atom. The bands are centered around 2070 cm^{-1}. The upfield shift from $\nu(CO) = 2003$ cm^{-1} in $W(CO)_6$[33] is typical of a change from a neutral to a cationic metal carbonyl. The bands at 690 and 395 cm^{-1} in Ia,b and at 650 and 285 cm^{-1} in Ic,d may be assigned as T_{1u} modes of the AsF_6^- and SbF_6^- ions, respectively.[34] The bands between 530 and 560 cm^{-1} are typical metal–carbon stretches. One other band appears at 318 cm^{-1} in all the IR spectra for the W compounds and at 325 cm^{-1} for the Mo compounds. This band can be assigned as a stretching mode for the short Se–Se bond. An Se–Se stretch of 310 cm^{-1} has been observed in $[Ir(dppe)_2Se_2]^+$.[25] The shift to higher wavenumber in I is indicative of an Se–Se bond order greater than 1, as discussed previously.[35]

All attempts to obtain Raman spectra for these compounds have failed. The compounds have a very dark color and do not scatter

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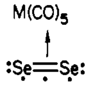
photons from a green 5145-Å source. Use of a red source results in rapid decomposition of the compound even at low temperature. Magnetic measurements of the solid by the Gouy method show the compound to be diamagnetic.

Bonding. The Se_2^+ ion can be described as having the electron configuration $(\sigma p_x)^2(\pi p_y)^2(\pi p_z)^2(\pi p^*_z)^1$, assuming that the interaction of the πp^*_y orbital with the metal atom raises its energy above that of the πp^*_z orbital.[36] We can then assume that the pair of electrons in the πp_y orbital is donated to $M(CO)_5$ to complete its 18-electron count, thus forming a 3-center–2-electron bond. This would result in the Se–Se bond having a resultant order of somewhere between 1.5 and 2.5, depending on the strength of the interaction with the metal atom, and probably slightly less than 2.0. Interaction of the p_z and p^*_z orbitals of two $M(CO)_5Se_2^+$ monomers then leads to the formation of a 4-center–6-electron bond.[6] MNDO calculations[37] on the related $S_6N_4^{2+}$ ion have shown that the interaction of the four p_z orbitals leads to the formation of four molecular orbitals (a_g, b_u, a_u, and b_g), with the six electrons occupying one bonding and two nonbonding orbitals of this set, thus giving rise to relatively weak bonding between two monomers. Alternatively, the bonding in Se_2^+, $M(CO)_5Se_2^+$, and $[M(CO)_5Se_2]_2^{2+}$ can be described in valence bond terms by structures **1**–**3**, respectively. In terms of this description the Se–Se bond order in **1** is 2.5, and in **2** and **3** it is ~2.

1



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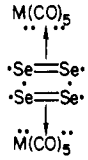

3

The recently reported I_4^{2+} cation consists of two I_2^+ monomers bonded together in a manner similar to that in the $[M(CO)_5Se_2]_2^{2+}$ dimer.[38] The formation of I_4^{2+} results in only a very small increase in the length of the I–I bond, which has an order of 1.5, from 2.557 Å in the monomer to 2.578 Å in the dimer. Presumably, therefore, the formation of the $[M(CO)_5Se_2]_2^{2+}$ dimer also results in only a very small increase in the Se–Se bond length from what it would be in the monomer. So the short Se–Se bond in the dimer can be regarded as having a bond order of ~2 in agreement with its length of only 2.21 Å.

Acknowledgment. This work was supported by a grant from the Natural Science and Engineering Research Council.

Registry No. Ia, 101935-11-9; Ib, 101935-13-1; Id, 101935-14-2; $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; $Cr(CO)_6$, 13007-92-6; $Se_4(AsF_6)_2$, 53513-64-7; $Se_8(AsF_6)_2$, 52374-78-4; $Se_{10}(SbF_6)_2$, 72827-63-5.

Supplementary Material Available: Listings of anisotropic thermal parameters and mean least-squares planes (3 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Texas at El Paso, El Paso, Texas 79968-0513

Dissociation Kinetics of 1,7-Diaza-4,10,13-trioxacyclopentadecane-*N*,*N'*-diacetic Acid Complexes of Lanthanides

V. Chandra Sekhar and C. Allen Chang*

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The dissociation kinetics of 1,7-diaza-4,10,13-trioxacyclopentadecane-*N*,*N'*-diacetic acid (K21DA) complexes of lanthanide(III) ions were studied in acetate–acetic acid buffer medium, over the acid concentration range of 8.4×10^{-6}–2.5×10^{-4} M and at a constant ionic strength of 0.1 M ($LiClO_4$). Copper(II) was used as the scavenger of free ligand, and the rates of dissociation of these complexes have been found to be independent of $[Cu^{2+}]$. All the complexes exhibit acid-independent and acid-dependent pathways. Lighter lanthanide complexes display a first-order dependence upon $[H^+]$ in the pH range studied. The complexes of heavier lanthanides show $[H^+]$ dependence at low acid concentrations but become acid-independent at high acid concentrations. Influence of acetate content in the buffer and total electrolyte concentration on the rate of dissociation has also been investigated. The observed rate constants for erbium, ytterbium, and lutetium complexes do not show a significant dependence on acetate concentration, but lanthanum and europium complexes do exhibit a first-order dependence on [acetate]. All the complexes under study respond similarly with change in electrolyte concentration; i.e., the rate constants decrease with increase in [electrolyte]. Activation parameters for both self-dissociation and acid-catalyzed dissociation pathways have been obtained for lanthanum, europium, erbium, and lutetium complexes, from the temperature dependence of rate constants in the 15–45 °C range. The results are compared with those of the lanthanide–polyamino polycarboxylate systems, and possible mechanisms are discussed.

Introduction

The majority of investigations concerning lanthanide complexes have been on their synthesis and structural studies,[1-7] thermodynamics of complexation,[8-12] analytical applications in separation of lanthanide ions,[13-16] and biological applications of metal–enzyme or protein bindings.[17-19] Comparatively very few studies have been devoted to their kinetics and reaction mechanisms[20-22] despite their significance in (i) improving the existing methods of lanthanide ion separations by ion exchange, solvent extraction, and other methods and (ii) understanding lanthanide metal ion exchange reactions in enzymes and proteins. The monodentate ligands in general are far too weak complexing agents[23] and, consequently, too labile to deduce a detailed reaction mechanism.

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