Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Formation and Structures of [Cs(18-crown-6)]$_2$[Se$_5$]·CH$_3$CN and [PPN]$_2$[Se$_4$]·4CH$_3$CN

Nathaniel E. Brese, Clayton R. Randall, and James A. Ibers*

Received July 7, 1987

Two compounds containing unbranched Se chains have resulted from the dissolution of Cs$_3$TaSe$_4$ in acetonitrile in the presence of 18-crown-6 and bis(triphenylphosphine)nitrogen(1+) chloride. These new compounds have been characterized by X-ray structure determinations. [Cs(18-crown-6)]$_2$[Se$_5$]·CH$_3$CN crystallizes in the monoclinic space group C_{2h}^2-$P2_1/m$, with a = 10.299 (6) Å, b = 15.097 (9) Å, c = 13.768 (8) Å, β = 100.05 (2)°, V = 2108 Å^3, and Z = 2. [PPN]$_2$[Se$_4$]·4CH$_3$CN crystallizes in the monoclinic space group C_{2h}^5-$P2_1/c$, with a = 10.792 (3) Å, b = 12.653 (4) Å, c = 26.209 (14) Å, β = 90.57 (3)°, V = 3579 Å^3, and Z = 2. The nonplanar Se$_5^{2-}$ chain has a cis configuration and crystallographic symmetry m, while the Se$_4^{2-}$ chain is planar and trans with a crystallographically imposed center of symmetry. A comparison of metrical data for these isolated ions with those for their free and liganded counterparts is provided.

Introduction

We have recently prepared several new ions that contain polyselenide chains. These include MoO(Se$_4$)$_2^{2-}$,[1] WS(Se$_4$)$_2^{2-}$,[1] (Se$_2$)WSe(Se)$_2$SeW(Se$_4$)$^{2-}$ (W$_2$Se$_{10}^{2-}$)[2] (all of which contain the Se$_4^{2-}$ bidentate ligand), and V$_2$(Se$_2$)$_4$(Se$_5$)$^{2-}$ (V$_2$Se$_{13}^{2-}$),[3] which contains the Se$_5^{2-}$ bidentate ligand. In an attempt to prepare the TaSe$_4^{3-}$ ion, we synthesized by high-temperature methods the compound Cs$_3$TaSe$_4$ and studied its dissolution at room temperature in acetonitrile in the presence of 18-crown-6 ether and large cations. To our surprise these dissolution studies yielded not salts of TaSe$_4^{3-}$ but rather new salts of the unliganded Se$_4^{2-}$ and Se$_5^{2-}$ ions. We report here the syntheses of these new salts, the structures of the isolated ions, and a comparison of metrical data for these isolated ions with those for their liganded counterparts.

Experimental Section

Cs$_3$TaSe$_4$. A 0.181-g (1.00-mmol) sample of tantalum powder (99.98%, AESAR) and 0.316 g (4.00 mmol) of selenium powder (99.99%, ALFA) were placed in a flame-dried fused silica tube. Inside a glovebox under an Ar atmosphere, 0.399 g (3.00 mmol) of liquid Cs (99.5%, AESAR) was added very slowly by pipet to the Ta/Se mixture. (*Caution*! The reaction is very exothermic.) The tube was then sealed under vacuum. It was next heated in a furnace at 800 °C for 8 days to afford Cs$_3$TaSe$_4$ as a yellow-green powder (95% yield). Anal. Calcd: Cs, 44.5; Ta, 20.2; Se, 35.3. Found: Cs, 43.9; Ta, 19.7; Se, 34.9. That a new compound has been prepared was established by refinement of neutron diffraction powder data.[4]

[Cs(18-crown-6)]$_2$[Se$_5$]·CH$_3$CN. A 0.201-g sample of Cs$_3$TaSe$_4$ (0.224 mmol), 0.1 g of benzoic acid (0.8 mmol), and 0.191 g of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) (0.723 mmol) were added to a 100-mL Schlenk flask in a glovebox under Ar. After 2 min the mixture turned brown. A 13.5-mL quantity of dry acetonitrile was added under N$_2$ with stirring. After 24 h the brown mixture was filtered to afford a dark green-brown filtrate and a gray solid. A 0.10-g sample of bis(triphenylphosphine)nitrogen(1+) chloride, (PPN)Cl (0.17 mmol), was added to 5.00 mL of the filtrate. After the solution was stirred for 30 min, its volume was reduced to about 3 mL by pumping. This mixture was cooled in a freezer for 2 weeks to −30 °C and then filtered cold to afford a dark green filtrate and a white solid. The solid was identified as CsCl by IR spectroscopy. A 1.10-mL portion of the filtrate was layered in a diffusion tube with 3.50 mL of dry ether, causing brown crystals, suitable for X-ray crystallographic analysis, to grow overnight. Analysis of three crystals with the microprobe of an EDAX-equipped Hitachi S-570 scanning electron microscope confirmed the presence of Cs and Se, as well as a trace amount of Ta (Ta:Se < 1:32) on the crystal surface. In addition, mass spectroscopy indicated the presence of a crown ether molecule and a pentaselenide chain. The composition of the material was ultimately established from an X-ray diffraction study of single crystals.

Table I. Summary of Crystal Data, Intensity Collection, and Refinements

compd	[Cs(crown)]$_2$[Se$_5$]·CH$_3$CN	[PPN]$_2$[Se$_4$]·4CH$_3$CN
formula	C$_{26}$H$_{51}$Cs$_2$NO$_{12}$Se$_5$	C$_{80}$H$_{72}$N$_6$P$_4$Se$_4$
mol wt	1230.04	1557.22
a, Å	10.299 (6)	10.792 (3)
b, Å	15.097 (9)	12.653 (4)
c, Å	13.768 (8)	26.209 (14)
β, deg	100.05 (2)	90.57 (3)
V, Å^3	2108	3579
Z	2	2
space group	C_{2h}^2-$P2_1/m$	C_{2h}^5-$P2_1/c$
T of data collcn, K	113[a]	113
density (calcd), g/cm^3	1.937	1.445
cryst vol, mm^3	0.0235	0.0071
cryst shape	flat plate bound by {001}, {110}	irregular plate bound by {010}, {001}, ($\bar{1}\bar{1}0$), ($\bar{1}00$), ($1\bar{1}0$)
radiation	graphite-monochromated Mo Kα (λ(Kα_1) = 0.709 30 Å)	
linear abs coeff, cm^{-1}	60.35	21.63
transmission factors	0.144–0.563[b]	0.648–0.781
detector aperture, mm	4 horiz, 1 vert, 17.3 cm from cryst	3 horiz, 3 vert, 17.3 cm from cryst
takeoff angle, deg	3.75	2.5
scan type	ω	ω
scan range, deg	±0.6 in ω	±0.7 in ω
scan speed, deg min^{-1}	2[c]	1.3 ($\theta < 20°$), 1 ($20 \leq \theta \leq 25°$)[d]
$\lambda^{-1} \sin \theta$ limits, Å^{-1}	0.0738–0.4239	0.0492–0.5958
bkgd counts	$^1/_4$ of scan range on each side of scan	
data collcd	$\pm h,\pm k,\pm l$	$+h,+k,\pm l$
p factor	0.04	0.04
no. of unique data, including $F_o^2 \leq 0$	1374[e]	6811
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	1254	1871[f]
no. of variables	171	189
$R(F^2)$	0.095	0.108
$R_w(F^2)$	0.129	0.128
R(on F for $F_o^2 > 3\sigma(F_o^2)$	0.052	0.070
error in observn of unit wt	2.41 e^2	1.36 e

[a] The low-temperature system for the Nonius CAD4-diffractometer is based on a design by Prof. J. J. Bonnet and S. Askenazy and is commercially available from Soterem, Z. T. de Vic, 31320 Castanet-Tolosan, France. [b] The analytical method, as employed in the Northwestern absorption program AGNOST, was used for the absorption correction (de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018). [c] Reflections for which $\sigma(I)/I > 0.3$ were rescanned for a maximum time of 100 s. [d] Reflections were not rescanned. [e] Final refinement on F^2. [f] Final refinement on F.

[PPN]$_2$[Se$_4$]·4CH$_3$CN. A 0.201-g sample of Cs$_3$TaSe$_4$ (0.224 mmol), 0.383 g of (PPN)Cl (0.669 mmol), and 0.177 g of 18-crown-6 ether (0.670 mmol) were addded to a 50-mL Schlenk flask in a glovebox under Ar. A 10.00-mL portion of dry acetonitrile was added under N$_2$ with stirring. After 18 h the yellow-green mixture was filtered to afford a

---

[1] Wardle, R. W. M.; Mahler, C. M.; Chau, C.-N.; Ibers, J. A., submitted for publication in *Inorg. Chem.*

[2] Wardle, R. W. M.; Chau, C.-N.; Ibers, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1859–1860.

[3] Chau, C.-N.; Wardle, R. W. M.; Ibers, J. A. *Inorg. Chem.* **1987**, *26*, 2740–2741.

[4] Yun, H.; Randall, C. R.; Ibers, J. A., submitted for publication in *J. Solid State Chem.*

0020-1669/88/1327-0940$01.50/0

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for [Cs(18-crown-6)]$_2$[Se$_5$]·CH$_3$CN

atom	*x*	*y*	*z*	B_{eq}, Å^2
Cs(1)	0.71545 (15)	$^1/_4$	0.11495 (12)	2.43 (6)
Cs(2)	0.77527 (17)	$^1/_4$	0.48826 (14)	3.55 (7)
Se(1)	0.43043 (26)	$^1/_4$	0.33015 (21)	3.1 (1)
Se(2)	0.47599 (18)	0.12564 (14)	0.24011 (15)	2.97 (7)
Se(3)	0.68682 (20)	0.07501 (14)	0.30112 (15)	3.18 (7)
O(1)	0.5085 (16)	$^1/_4$	0.9045 (12)	3.0 (6)
O(2)	0.6300 (12)	0.08839 (80)	0.97823 (96)	3.3 (4)
O(3)	0.9051 (12)	0.09290 (82)	0.05639 (97)	3.4 (5)
O(4)	0.0193 (15)	$^1/_4$	0.1455 (13)	3.1 (6)
C(1)	0.4290 (18)	0.1740 (14)	0.9176 (14)	3.1 (7)
C(2)	0.5153 (21)	0.0925 (16)	0.9010 (16)	4.9 (8)
C(3)	0.7199 (19)	0.0177 (15)	0.9657 (15)	3.5 (5)
C(4)	0.8260 (18)	0.0146 (14)	0.0550 (15)	3.5 (5)
C(5)	0.0063 (19)	0.0931 (14)	0.1419 (17)	4.1 (8)
C(6)	0.0965 (18)	0.1729 (15)	0.1335 (15)	3.8 (5)
O(5)	0.5984 (53)	0.3264 (45)	0.6178 (22)	38 (5)
O(6)	0.8483 (31)	0.4421 (19)	0.6156 (16)	20 (1)
O(7)	0.0916 (31)	0.1817 (32)	0.5238 (21)	39 (4)
C(7)	0.4923 (40)	0.1743 (31)	0.6242 (32)	13 (1)
C(8)	0.5819 (45)	0.4145 (28)	0.6125 (32)	13 (1)
C(9)	0.6935 (44)	0.4513 (26)	0.5983 (29)	12 (1)
C(10)	0.9844 (36)	0.4377 (23)	0.6111 (29)	18 (1)
C(11)	0.0934 (44)	0.3498 (34)	0.6155 (43)	17 (2)
N(1)	1.0900 (32)	$^1/_4$	0.8701 (26)	10 (2)
C(13)	0.9654 (58)	$^1/_4$	0.8530 (29)	7 (2)
C(14)	0.8264 (32)	$^1/_4$	0.8365 (37)	9 (2)

Table III. Positional Parameters and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of [PPN]$_2$[Se$_4$]·4CH$_3$CN

atom	*x*	*y*	*z*	*B*, Å^2
Se(1)	0.10886 (19)	0.51146 (17)	0.493228 (73)	1.73 (4)
Se(2)	0.19880 (20)	0.09105 (18)	0.056535 (75)	1.98 (5)
P(1)	−0.25233 (45)	0.10411 (41)	0.28466 (17)	1.0 (1)
P(2)	−0.50281 (42)	0.09476 (43)	0.32948 (17)	0.9 (1)
N(1)	−0.3942 (13)	0.1305 (11)	0.29298 (47)	1.0 (3)
C(1)	−0.2087 (16)	−0.0310 (14)	0.29845 (60)	1.2 (4)
C(2)	−0.1402 (15)	−0.0556 (13)	0.34207 (60)	0.8 (3)
C(3)	−0.1193 (19)	−0.1606 (16)	0.35296 (73)	2.0 (4)
C(4)	−0.1632 (16)	−0.2424 (14)	0.32137 (63)	1.1 (4)
C(5)	−0.2322 (16)	−0.2128 (15)	0.27885 (64)	1.3 (4)
C(6)	−0.2553 (15)	−0.1111 (14)	0.26668 (58)	0.4 (3)
C(7)	−0.2189 (16)	0.1272 (14)	0.21904 (64)	1.1 (4)
C(8)	−0.2881 (18)	0.2010 (16)	0.19148 (70)	1.9 (4)
C(9)	−0.2606 (18)	0.2225 (16)	0.14151 (70)	1.7 (4)
C(10)	−0.1658 (17)	0.1723 (15)	0.11792 (65)	0.9 (4)
C(11)	−0.0933 (14)	0.1007 (14)	0.14425 (57)	0.7 (3)
C(12)	−0.1239 (15)	0.0765 (13)	0.19474 (62)	1.3 (3)
C(13)	−0.1528 (17)	0.1917 (14)	0.32123 (63)	1.3 (4)
C(14)	−0.0284 (17)	0.2004 (15)	0.31022 (64)	1.5 (4)
C(15)	0.0448 (18)	0.2669 (15)	0.33849 (69)	1.9 (4)
C(16)	−0.0052 (18)	0.3249 (15)	0.37811 (68)	1.5 (4)
C(17)	−0.1278 (18)	0.3138 (14)	0.38951 (65)	1.3 (4)
C(18)	−0.2026 (16)	0.2491 (14)	0.36109 (63)	1.6 (4)
C(19)	−0.4594 (14)	0.0003 (14)	0.37688 (55)	0.6 (3)
C(20)	−0.4637 (17)	−0.1083 (15)	0.36714 (64)	1.4 (4)
C(21)	−0.4130 (18)	−0.1758 (16)	0.40207 (71)	2.0 (4)
C(22)	−0.3619 (18)	−0.1430 (15)	0.44701 (67)	1.5 (4)
C(23)	−0.3596 (18)	−0.0360 (15)	0.45798 (69)	1.6 (4)
C(24)	−0.4074 (17)	0.0360 (15)	0.42269 (67)	1.8 (4)
C(25)	−0.6256 (15)	0.0368 (12)	0.29033 (56)	0.6 (3)
C(26)	−0.7336 (16)	0.0003 (16)	0.31345 (63)	1.7 (4)
C(27)	−0.8273 (19)	−0.0428 (16)	0.28168 (73)	2.3 (5)
C(28)	−0.8101 (16)	−0.0469 (13)	0.23022 (63)	1.3 (4)
C(29)	−0.7048 (17)	−0.0076 (16)	0.20721 (62)	1.7 (4)
C(30)	−0.6110 (16)	0.0333 (14)	0.23854 (62)	1.1 (4)
C(31)	−0.5685 (16)	0.2097 (14)	0.35960 (60)	1.0 (4)
C(32)	−0.5370 (16)	0.3084 (14)	0.34112 (61)	1.5 (4)
C(33)	−0.5861 (16)	0.3982 (15)	0.36156 (61)	1.3 (4)
C(34)	−0.6675 (16)	0.3902 (15)	0.40210 (64)	1.9 (4)
C(35)	−0.6966 (17)	0.2913 (15)	0.42289 (63)	1.7 (4)
C(36)	−0.6453 (16)	0.2004 (14)	0.40122 (60)	0.9 (4)
N(2)	0.0989 (17)	0.0464 (15)	0.43149 (66)	4.3 (5)
C(37)	0.0528 (19)	0.1058 (17)	0.46116 (74)	2.9 (5)
C(38)	−0.0007 (24)	0.1748 (17)	0.49836 (89)	3.6 (5)
N(3)	−0.3138 (17)	0.2969 (16)	0.01038 (66)	4.3 (5)
C(39)	−0.3638 (20)	0.2191 (18)	0.00751 (74)	2.8 (5)
C(40)	−0.4298 (21)	0.1213 (19)	0.00711 (80)	4.7 (6)

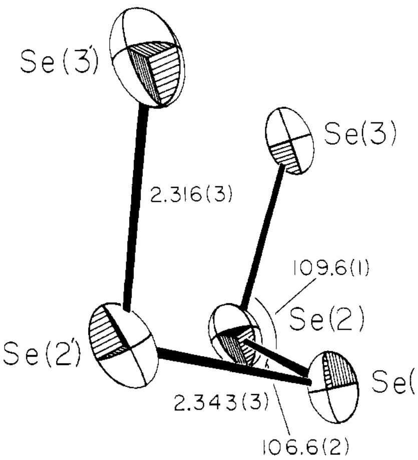

Figure 1. View of the Se$_5^{2-}$ ion in [Cs(18-crown-6)]$_2$[Se$_5$]·CH$_3$CN. Thermal ellipsoids in this figure and in Figure 2 are shown at their 50% values.

Table V. Selected Bond Distances (Å) and Angles (deg) for [Cs(18-crown-6)]$_2$[Se$_5$]·CH$_3$CN

Cs(1)–O(4)	3.08 (1)	Se(1)–Se(2)	2.343 (3)
Cs(1)–O(2)	3.11 (1)	Se(2)–Se(3)	2.316 (3)
Cs(1)–O(3)	3.26 (1)	O(1)–C(1)	1.44 (2)
Cs(1)–O(1)	3.28 (2)	O(2)–C(2)	1.45 (2)
Cs(2)–O(5)	2.99 (3)	O(2)–C(3)	1.44 (2)
Cs(2)–O(7)	3.37 (3)	O(3)–C(4)	1.43 (2)
Cs(2)–O(6)	3.41 (3)	O(3)–C(5)	1.43 (2)
Cs(1)–Se(3)	3.730 (3)	O(4)–C(6)	1.44 (2)
Cs(1)–Se(2)	3.751 (3)	C(1)–C(2)	1.56 (3)
		C(3)–C(4)	1.50 (3)
Cs(2)–Se(3)	3.693 (2)	C(5)–C(6)	1.54 (3)
Cs(2)–Se(1)	3.826 (3)	C(13)–N(1)	1.26 (5)
		C(13)–C(14)	1.41 (5)
Se(2)–Se(1)–Se(2′)	106.6 (2)	O(2)–C(3)–C(4)	108 (2)
Se(1)–Se(2)–Se(3)	109.6 (1)	C(3)–C(4)–O(3)	108 (2)
C(1)–O(1)–C(1′)	106 (2)	O(3)–C(5)–C(6)	108 (2)
C(2)–O(2)–C(3)	114 (2)	C(5)–C(6)–O(4)	106 (1)
C(4)–O(3)–C(5)	110 (1)	N(1)–C(13)–C(14)	179 (4)
C(6)–O(4)–C(6′)	108 (2)	Se(3)–Se(2)–Se(1)–Se(2′)	96.3 (1)[a]
O(1)–C(1)–C(2)	105 (1)		
C(1)–C(2)–O(2)	110 (2)		

[a] A clockwise rotation of 96.3° of Se(3) about the bond from Se(2) to Se(1) superimposes it on Se(2′).

brown filtrate and a white solid. The volume of the filtrate was reduced to about 5 mL by pumping, and 5.00 mL of dry toluene was added. This mixture was cooled in a freezer overnight to −30 °C and then filtered cold to afford a brown filtrate and more white solid. An aliquot of this filtrate was layered in a diffusion tube with dry ether, causing dark red-brown crystals, suitable for X-ray crystallographic analysis, to grow overnight. Microprobe analysis of two single crystals revealed the presence of P and Se but not Ta or Cs. The composition of these crystals was ultimately established from the X-ray structure analysis.

Crystallographic Studies

Examination of intensity data for the compound [Cs(18-crown-6)]$_2$[Se$_5$]·CH$_3$CN revealed only one systematic absence ($0k0$, k odd), which is consistent with the space groups C_2^2-$P2_1$ and C_{2h}^2-$P2_1/m$. As a satisfactory residual of 3.0% results from averaging those absorption corrected data equivalent in $P2_1/m$, that space group was chosen. The unit cell parameters were determined from least-squares analysis of 25 reflections in the range 24.1° < 2θ(Mo Kα_1) < 35.5° that had been automatically centered on an Enraf-Nonius CAD4 X-ray diffractometer. Additional relevant crystal data and details of data collection are given in Table I.

All calculations were performed on a Harris 1000 computer with methods and programs standard for this laboratory.[5] The

---

(5) Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

Table VI. Se–Se Bond Distances (Å) and Angles (deg) for Representative Pentaselenides[a]

	chains				ring
	$[Cs(crown)]_2[Se_5]$[b]	$Cs_2[Se_5]$[c]	$Rb_2[Se_5]$[d]	$Fe_2Se_2(Se_5)_2$[e]	$V_2Se_{13}^{2-}$[f]
Se(1)–Se(2)	2.316 (3)	2.33 (1)	2.31 (2)	2.345 (2)	2.425 (3)
Se(2)–Se(3)	2.343 (3)	2.38 (1)	2.36 (1)	2.318 (2)	2.360 (3)
Se(3)–Se(4)	2.343 (3)	2.34 (1)	2.37 (2)	2.337 (2)	2.339 (3)
Se(4)–Se(5)	2.316 (3)	2.29 (1)	2.33 (1)	2.347 (2)	2.431 (3)
Se(1)–Se(2)–Se(3)	109.6 (1)	107.2 (4)	109.1 (5)	104.05 (6)	107.4 (1)
Se(2)–Se(3)–Se(4)	106.6 (2)	104.6 (4)	104.5 (6)	103.35 (7)	103.4 (1)
Se(3)–Se(4)–Se(5)	109.6 (1)	110.8 (4)	108.0 (5)	104.27 (7)	107.3 (1)

[a] Numbered Se(1)–Se(2)–Se(3)–Se(4)–Se(5). [b] Present work. [c] Reference 12. [d] Reference 13. [e] Reference 14. [f] Reference 3.

Table VII. Selected Bond Lengths (Å) and Bond Angles (deg) for $[PPN]_2[Se_4]\cdot4CH_3CN$

Se(1)–Se(2)	2.312 (3)	P(2)–C(25)	1.822 (16)
Se(1)–Se(1′)[a]	2.397 (4)	P(2)–C(31)	1.803 (18)
P(1)–N(1)	1.584 (14)	C–C (Ph)	1.383 (16)[b]
P(2)–N(1)	1.586 (14)	N(2)–C(37)	1.194 (24)
P(1)–C(1)	1.809 (18)	N(3)–C(39)	1.124 (25)
P(1)–C(7)	1.785 (17)	C(37)–C(38)	1.434 (28)
P(1)–C(13)	1.811 (18)	C(39)–C(40)	1.429 (28)
P(2)–C(19)	1.783 (16)		
Se(2)–Se(1)–Se(1′)	103.4 (1)	C(1)–P(1)–C(7)	107.0 (8)
P(1)–N(1)–P(2)	138.1 (9)	C(1)–P(1)–C(13)	108.7 (8)
N(1)–P(1)–C(1)	115.0 (8)	C(7)–P(1)–C(13)	106.6 (8)
N(1)–P(1)–C(7)	107.6 (8)	C(19)–P(2)–C(25)	107.9 (8)
N(1)–P(1)–C(13)	111.5 (8)	C(19)–P(2)–C(31)	109.7 (8)
N(1)–P(2)–C(19)	114.9 (7)	C(25)–P(2)–C(31)	106.5 (8)
N(1)–P(2)–C(25)	108.2 (7)	N(2)–C(37)–C(38)	178 (2)
N(1)–P(2)–C(31)	109.7 (8)	N(3)–C(39)–C(40)	176 (2)

[a] Se(1′) is related to Se(1) by a crystallographic center of symmetry. [b] Average of 36 C–C distances in the six phenyl rings of the PPN cation. The estimated standard deviation in parentheses is of a single observation on the assumption that the numbers averaged are from the same population. That this is slightly smaller than those estimated from the inverse matrix suggests that overall the estimates of standard deviations are reliable.

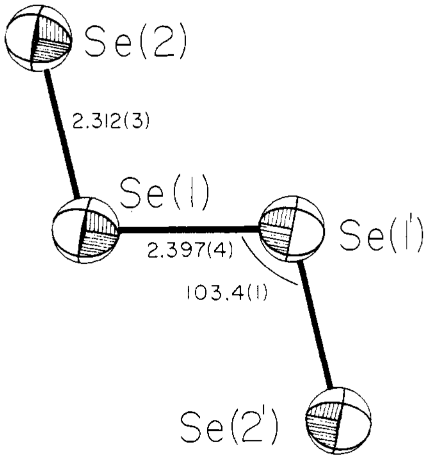

Figure 2. View of the Se_4^{2-} ion in $[PPN]_2[Se_4]\cdot4CH_3CN$.

initial Cs and Se positions, as well as those of the atoms in the first crown ether molecule, were determined by direct methods. The remaining crown ether molecule and the acetonitrile were located by use of the DIRDIF program.[6] Since this second crown ether molecule is disordered, as evidenced by large thermal parameters (some $B_{eq} > 30$ Å^2 for data collected at 113 K!), hydrogen positions were neither calculated nor refined, and one of the C atoms could not be located. Details of the refinement are provided in Table I. A final difference electron density map reveals no features greater than 1.7% of the height of a Cs atom. An analysis of F_o^2 vs F_c^2 as a function of $\lambda^{-1} \sin \theta$, F_o^2, and Miller indices reveals no unusual trends. Apparently the disorder of the crown ether molecule was modeled successfully by the use of anisotropic thermal parameters. Final positional parameters are given in Table II.

Examination of intensity data for the compound $[PPN]_2[Se_4]\cdot4CH_3CN$ reveals absences ($0k0$, k odd; $h0l$, l odd) that are consistent with the space group C_{2h}^5-$P2_1/c$. Unit cell parameters were determined from the least-squares analysis of 25 reflections in the range 22° $\leq 2\theta$(Mo Kα_1) $\leq$ 26° that had been automatically centered on a CAD4 diffractometer.

The structure was solved by a combination of Patterson and direct methods. Refinement proceeded smoothly. Hydrogen atoms were added as fixed contributions to F_c in the final refinement. Their positions were idealized on the assumption of C–H = 0.95 Å and $B_H = B_C + 1.0$ Å^2. The methyl hydrogen atoms on the solvent molecules were located in a difference electron density map and idealized. The refinement was terminated at the isotropic model owing to the limited number of significant data from the very small crystal and to the fact that thermal motion is not large. A final difference electron density map displays no features above 2% the height of a Se atom in the structure. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of setting angles and Miller indices reveals no unusual trends. Final positional parameters are presented in Table III. In Table IV[7] are found anisotropic thermal parameters and structure amplitudes for the Se_5^{2-} salt as well as hydrogen atom positions and structure amplitudes for the Se_4^{2-} salt.

Results and Discussion

No salts of the $TaSe_4^{3-}$ ion resulted from the dissolution of Cs_3TaSe_4 in acetonitrile in the presence of 18-crown-6 (to chelate the Cs^+ ion) and PPN^+. Rather, salts of polyselenide ions were obtained. Dissolution of a solid-state selenide to afford salts of polyselenide ions is not without precedent. König, Eisenmann, and Schäfer dissolved $BaBiSe_3$, a material with a well-defined, extended solid-state structure, in ethylenediamine in the presence of 2,2,2-crypt to obtain Ba(crypt)$[Se_4]\cdot$en.[8] The compound Cs_3TaSe_4 contains discrete $TaSe_4^{3-}$ ions.[4] Yet depending upon conditions, its dissolution in CH_3CN affords the salts $[Cs(18\text{-crown-}6)]_2[Se_5]\cdot CH_3CN$ and $[PPN]_2[Se_4]\cdot4CH_3CN$. Pathways by which these form are unknown.

Selected bond distances and angles for $[Cs(18\text{-crown-}6)]_2[Se_5]\cdot CH_3CN$ are provided in Table V. A perspective view of the Se_5^{2-} unit perpendicular to the crystallographically imposed mirror plane is displayed in Figure 1.

Each Cs atom is associated with a crown ether molecule and an Se_5^{2-} chain. Atom Cs(1) has ten interactions less than 4 Å (six oxygen, four selenium) while atom Cs(2) has nine (six oxygen, three selenium). The six Cs(1)–O distances are more regular than those reported previously[9] (3.08 (1)–3.28 (2) vs 3.09 (3)–3.69 (2) Å). In addition, the C–O and C–C distances within that crown ether molecule are in good agreement with those reported pre-

---

(6) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van den Hark, T. E. M.; Prick, P. A. J.; Noordik, J. H.; Beurskens, G.; Parthasarathi, V., "DIRDIF 81"; Crystallography Laboratory, Toernooiveld: Nijmegen, The Netherlands, 1981.

(7) See paragraph at end of paper regarding supplementary material.

(8) König, V. T.; Eisenmann, B.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1983**, *498*, 99–104.

(9) Vidal, J. L.; Schoening, R. C.; Troup, J. M. *Inorg. Chem.* **1981**, *20*, 227–238.

Table VIII. Se–Se Bond Distances (Å) and Angles (deg) for Representative Tetraselenides

materials	Se(1)–Se(2)	Se(2)–Se(3)	Se(3)–Se(4)	Se(1)–Se(2)–Se(3)	Se(2)–Se(3)–Se(4)
		Chains			
$[\mathrm{PPN}]_2[\mathrm{Se_4}]\cdot 4\mathrm{CH_3CN}$[a]	2.312 (3)	2.397 (4)	2.312 (3)	103.4 (1)	103.4 (1)
$[\mathrm{Ba\text{-}222Crypt}][\mathrm{Se_4}]$[b]	2.325 (5)	2.344 (5)	2.325 (5)	110.7 (1)	113.9 (1)
$[\mathrm{Ba\text{-}4en}][\mathrm{Se_4}]$[c]	2.329 (3)	2.342 (4)	2.329 (3)	112.1 (1)	112.1 (1)
$(\mathrm{NC_4H_8O})_2[\mathrm{Se_4}]$[d]	2.336 (2)	2.356 (2)	2.336 (2)	102.1 (1)	102.1 (1)
$(\mathrm{NC_5H_{10}})_2[\mathrm{Se_4}]$[d]	2.327 (2)	2.347 (2)	2.327 (2)	104.1 (1)	104.1 (1)
		Rings			
$\mathrm{MoO(Se_4)_2^{2-}}$[e]	2.390 (1)	2.303 (2)	2.446 (2)	99.31 (5)	98.51 (5)
	2.425 (1)	2.304 (2)	2.399 (2)	98.41 (5)	97.68 (5)
$\mathrm{W_2Se_{10}^{2-}}$[f]	2.316 (4)	2.281 (5)	2.328 (5)	95.3 (2)	99.7 (2)
$\mathrm{WS(Se_4)_2^{2-}}$[g]	2.419 (2)	2.301 (2)	2.458 (2)	100.57 (6)	98.94 (5)
	2.416 (2)	2.300 (2)	2.514 (2)	102.26 (6)	100.51 (6)
$[\mathrm{Ir(Se_4)(dmpe)_2}]^-$[h]	2.340 (3)	2.301 (5)	2.340 (3)	97.5 (1)	97.5 (1)
	2.305 (4)	2.251 (7)	2.305 (4)	101.4 (2)	101.4 (2)

[a] Present work. [b] Reference 8. [c] Reference 15. [d] Reference 16. [e] Reference 1. [f] Reference 2. [g] Reference 1. [h] Reference 17.

viously[10] (1.43 (2)–1.45 (2), 1.50 (3)–1.56 (3) vs 1.418 (1)–1.430 (1), 1.506 (1)–1.512 (1) Å). Since the crown ether molecule associated with atom Cs(2) is disordered, the Cs(2)–O distances are unreliable. Addition of ionic radii[11] predicts a Cs–Se bond length of 3.79 Å. The Cs(1) atom interacts with two Se(2) atoms and two Se(3) atoms (3.751 (3), 3.730 (3) Å), while the Cs(2) atom interacts with two Se(3) atoms and one Se(1) atom (3.693 (2), 3.826 (3) Å).

No unusual bond lengths were found for the $\mathrm{Se_5^{2-}}$ chain. The chain has a cis conformation whereas all previously reported, unliganded $\mathrm{Se_5^{2-}}$ chains have trans conformations. Table VI presents bond lengths and angles for representative $\mathrm{Se_5^{2-}}$ units, both chains and rings.[4,12–14]

Table VII presents selected bond distances and angles for $[\mathrm{PPN}]_2[\mathrm{Se_4}]\cdot 4\mathrm{CH_3CN}$. The compound contains an $\mathrm{Se_4^{2-}}$ chain that has a crystallographically imposed center of symmetry. Accordingly, it is planar and has a trans configuration. A view of this $\mathrm{Se_4^{2-}}$ ion is displayed in Figure 2. Bond lengths and angles for representative $\mathrm{Se_4^{2-}}$ units, both chains and rings, are given in Table VIII.[1–3,8,15–17] In the present $\mathrm{Se_4^{2-}}$ ion the terminal bond (2.312 (3) Å) is slightly shorter than those reported for similar $\mathrm{Se_4^{2-}}$ chains, while the internal bond is significantly longer (2.397 (4) Å). Other distances in the structure are unexceptional.

In systems devoid of metal atoms, the $\mathrm{S_4^{2-}}$ ion exhibits an interesting alternation of bond lengths;[18] the internal bond length is longer than the external ones. Conversely, the bidentate $\mathrm{S_4^{2-}}$ ligand in the Mo–S system[19] exhibits a longer terminal bond length (>0.10 Å). Block and Allmann proposed that significant Mo-(d$_\pi$)–S(d$_\pi$) interactions force this change in the alternation of S–S bond lengths.[20] As the terminal ends of the $\mathrm{S_4^{2-}}$ ligand are drawn toward the Mo atom, they are pulled away from the internal S atoms, thereby reversing the alternation of bond lengths.

The data in Table VIII show a similar trend for liganded and unliganded chains in the Se system. SCF–Sα–SW calculations on $[\mathrm{Ir(Se_4)(PH_3)_4}]^+$ indicate that there is significant overlap of the Se 4p orbitals with the 5d$_{yz}$, 5d$_{z^2}$, and 6p$_x$ orbitals of Ir.[17] The $\mathrm{Se_4^{2-}}$ ligand itself is held together by pσ bonds, and a bond order of 1.15 was calculated for the internal Se–Se bond. As a free chain, $\mathrm{Se_4^{2-}}$ is held together by single pσ bonds. Thus, unliganded $\mathrm{Se_4^{2-}}$ ion has an opposite long–short alternation from the liganded $\mathrm{Se_4^{2-}}$ ion.

Acknowledgment. This research was supported by the National Science Foundation, Grant CHE87-01007. Use was made of the Scanning Electron Microscope Facility of Northwestern University's Material Research Center, supported in part under the NSF-MRL program Grant DMR85-20280.

Registry No. $\mathrm{Cs_3TaSe_4}$, 112087-91-9; $[\mathrm{Cs(18\text{-}crown\text{-}6)}]_2[\mathrm{Se_5}]\cdot\mathrm{CH_3CN}$, 112087-93-1; $[\mathrm{PPN}]_2[\mathrm{Se_4}]\cdot 4\mathrm{CH_3CN}$, 112087-95-3; Ta, 7440-25-7; Se, 7782-49-2; Cs, 7440-46-2.

Supplementary Material Available: Table IV, listing anisotropic thermal parameters for the $\mathrm{Se_5^{2-}}$ salt, hydrogen atom positions for the $\mathrm{Se_4^{2-}}$ salt (2 pages), and structure amplitudes (×10) for both compounds (14 pages). Ordering information is given on any current masthead page.

---

(10) Maverick, E.; Seiler, P.; Schweizer, W. B.; Dunitz, J. D. *Acta. Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 615–620.

(11) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751–767.

(12) Kretschmann, U.; Böttcher, P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 895–899.

(13) Böttcher, P. *Z. Kristallogr.* **1979**, *150*, 65–73.

(14) Strasdeit, H.; Krebs, B.; Henkel, G. *Inorg. Chim. Acta* **1984**, *89*, L11–L13.

(15) König, T.; Eisenmann, B.; Schäfer, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1245–1249.

(16) Foss, O.; Janickis, V. *J. Chem. Soc., Dalton Trans.* **1980**, 620–623.

(17) Ginsberg, A. P.; Osborne, J. H.; Sprinkle, C. R. *Inorg. Chem.* **1983**, *22*, 1781–1790.

(18) (a) Barrick, J. C.; Calvo, C.; Olsen, F. P. *Can. J. Chem.* **1973**, *51*, 3691–3696. (b) Ahmed, F. R.; Przybylska, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 168–170. (c) Gilardi, R.; Flippen-Anderson, J. L. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *C41*. 72–76.

(19) (a) Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baenziger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321–3332. (b) Simhon, E. D.; Baenziger, N. C.; Kanatzidis, M.; Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1981**, *103*, 1218–1219.

(20) Block, H. D.; Allmann, R. *Cryst. Struct. Commun.* **1975**, *4*, 53–56.