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New Inclusion Compounds of Selenourea with Tetraethyl- and Tetra-*n*-propylammonium Halides

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Abstract

Air-sensitive selenourea inclusion complexes tetraethylammonium chloride–selenourea (1/2), $(C_2H_5)_4N^+.Cl^-.2[(NH_2)_2CSe]$ (1), tetra-*n*-propylammonium chloride–selenourea (1/3), $(n\text{-}C_3H_7)_4N^+.Cl^-.3[(NH_2)_2CSe]$ (2), tetra-*n*-propylammonium bromide–selenourea (1/3), $(n\text{-}C_3H_7)_4N^+.Br^-.3[(NH_2)_2CSe]$ (3), and tetra-*n*-propylammonium iodide–selenourea (1/1), $(n\text{-}C_3H_7)_4N^+.I^-.(NH_2)_2CSe$ (4), have been prepared and characterized by X-ray crystallography. Crystal data, Mo $K\alpha$ radiation: (1), space group $P2_1/n$, $Z = 4$, $a = 8.768\,(5)$, $b = 11.036\,(6)$, $c = 19.79\,(1)$ Å, $\beta = 96.92\,(1)°$, $R_F = 0.055$ for 1468 observed data; (2), space group Cc, $Z = 4$, $a = 18.091\,(4)$, $b = 13.719\,(3)$, $c = 11.539\,(2)$ Å, $\beta = 111.93\,(3)°$, $R_F = 0.051$ for 1187 observed data; (3), space group Cc, $Z = 4$, $a = 18.309\,(4)$, $b = 13.807\,(3)$, $c = 11.577\,(2)$ Å, $\beta = 112.45\,(3)°$, $R_F = 0.049$ for 1592 observed data; (4), space group $P2_1/n$, $Z = 4$, $a = 8.976\,(1)$, $b = 14.455\,(2)$, $c = 15.377\,(3)$ Å, $\beta = 94.16\,(1)°$, $R_F = 0.062$ for 1984 observed data. In the crystal structure of (1) the parallel alternate arrangement of selenourea–chloride ribbons and selenourea chains generates a puckered layer and the cations are sandwiched between them. In the isomorphous complexes (2) and (3) wide selenourea–halide double ribbons are crosslinked by bridging selenourea molecules *via* N—H···Se and N—H···*X* hydrogen bonds [average N···Se = 3.521 (8) and 3.527 (7), N···Cl = 3.354 (8) and N···Br = 3.500 (7) Å in (2) and (3), respectively] to form a channel-like three-dimensional network and the cations are accommodated in a single column within each channel. In the crystal structure of (4) the selenourea molecules are joined in the shoulder-to-shoulder fashion *via* N—H···Se hydrogen bonds [N···Se = 3.529 (7) and 3.534 (7) Å] to generate a ribbon and each selenourea molecule also forms a pair of chelating N—H···I hydrogen bonds [N···I = 3.567 (7) and 3.652 (7) Å] to an adjacent iodide ion.

1. Introduction

Selenourea, like urea and thiourea, can form channel-type inclusion compounds with a variety of hydrocarbons. Its inclusion properties were studied by van Bekkum and coworkers (van Bekkum, Remijnse & Wepster, 1969) well over 20 years after the discovery of the analogous urea (Bengen, 1940) and thiourea (Angla, 1947) inclusion compounds. The structures of adamantane inclusion complexes with thiourea and selenourea were also reported in 1989 (Gopal, Robertson & Rutherford, 1989). Although the difference in channel diameter between thiourea and selenourea inclusion compounds is small, selenourea seems to be much more selective in its choice of guest molecules (Takemota & Sonoda, 1984). There are more striking differences in the unit-cell dimensions of the selenourea inclusion compounds than are observed for the thiourea inclusion compounds, as adaptation of the selenourea lattice to the shape and size of the included molecules is apparently relatively easy (Nicolaides & Laves, 1958; Barlow & Corish, 1959; Casu, 1961). A theoretical study of the conformations and vibrational frequencies in urea, thiourea and selenourea compounds has been reported (Ha & Puebla, 1994). Studies on the complexation of Tl^+ with I^- and urea, thiourea or selenourea (and their Me derivatives) using a horizontal zone electromigration method have indicated that the complexing capacities of the urea derivatives increase in the order urea < thiourea < *N*,*N*,*N'*,*N'*-tetramethylthiourea < selenourea (Frind, Scheibe, Fischer, Ross & Dreyer, 1991).

In our design of new urea/thiourea–anion host lattices containing hydrophobic, bulky organic cations as templates, some simple trigonal planar oxo-anions that can easily form O···H—N acceptor hydrogen bonds, such as CO_3^{2-}, NO_3^-, HCO_3^- and H_3BO_3, have been used as building blocks and the crystal structures of urea–allophanate (Mak, Yip & Li, 1995), thiourea–bicarbonate (Li & Mak, 1995) and thiourea–nitrate (Li & Mak, 1996*a*) complexes have been reported by us recently. Some monocarboxylic acid radicals, such as HCO_2^- (Li & Mak, 1997*a*) and $CH_3CO_2^-$ (Li & Mak, 1997*b*), and dicarboxylic acid radicals, such as hydrogen oxalate $HC_2O_4^-$ and hydrogen fumarate $HC_4H_2O_4^-$, have also been used as the anionic components (Li & Mak, 1997*c*). The combined use of selenourea and other molecular species as the building blocks provides an opportunity to investigate

Table 1. *Experimental details*

Crystal data				
Chemical formula	$(C_2H_5)_4N^+.Cl^-.2[(NH_2)CSe]$	$(C_3H_7)_4N^+.Cl^-.3[(NH_2)CSe]$	$(C_3H_7)_4N^+.Br^-.3[(NH_2)CSe]$	$(C_3H_7)_4N^+.I^-.(NH_2)_2CSe$
Chemical formula weight	411.7	590.9	635.3	436.3
Cell setting	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	Cc	Cc	$P2_1/n$
a (Å)	8.768 (5)	18.091 (4)	18.309 (4)	8.976 (1)
b (Å)	11.036 (6)	13.719 (3)	13.807 (3)	14.455 (2)
c (Å)	19.79 (1)	11.539 (2)	11.577 (2)	15.377 (3)
β (°)	96.92 (4)	111.93 (3)	112.45 (3)	94.16 (1)
V (Å^3)	1901 (2)	2656.6 (9)	2705 (1)	1989.9 (4)
Z	4	4	4	4
D_x (Mg m^{-3})	1.438	1.477	1.560	1.456
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25	25
θ range (°)	6–14	6–14	6–14	6–14
μ (mm^{-1})	0.403	0.427	0.557	0.343
Temperature (K)	291	291	291	291
Crystal form	Block	Plate	Plate	Plate
Crystal size (mm)	0.28 × 0.22 × 0.20	0.50 × 0.42 × 0.42	0.42 × 0.32 × 0.26	0.42 × 0.40 × 0.36
Crystal color	Colorless	Colorless	Colorless	Colorless
Data collection				
Diffractometer	Siemens P4	Siemens P4	Siemens P4	Siemens P4
Data collection method	ω scans	ω scans	ω scans	ω scans
Absorption correction	ψ scans (Kopfmann & Huber, 1968)	ψ scans (Kopfmann & Huber, 1968)	ψ scans (Kopfmann & Huber, 1968)	ψ scans (Kopfmann & Huber, 1968)
$T_{\min}$	0.284	0.684	0.624	0.439
$T_{\max}$	0.581	0.993	1.000	0.848
No. of measured reflections	2871	2228	4828	4118
No. of independent reflections	2671	2121	3464	3867
No. of observed reflections	1468	1187	1592	1984
Criterion for observed reflections	$\|F_o\|>4\sigma(\|F_o\|)$	$\|F_o\|>4\sigma(\|F_o\|)$	$\|F_o\|>4\sigma(\|F_o\|)$	$\|F_o\|>4\sigma(\|F_o\|)$
$R_{\rm int}$	0.036	0.024	0.169	0.033
$\theta_{\max}$ (°)	25	25	25	26
Range of h, k, l	$0 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 12$ $-21 \rightarrow l \rightarrow 21$	$0 \rightarrow h \rightarrow 20$ $0 \rightarrow k \rightarrow 15$ $-13 \rightarrow l \rightarrow 12$	$0 \rightarrow h \rightarrow 21$ $0 \rightarrow k \rightarrow 16$ $-14 \rightarrow l \rightarrow 13$	$0 \rightarrow h \rightarrow 11$ $0 \rightarrow k \rightarrow 17$ $-18 \rightarrow l \rightarrow 18$
No. of standard reflections	3	3	3	3
Frequency of standard reflections	Every 97 reflections	Every 97 reflections	Every 97 reflections	Every 97 reflections
Refinement				
Refinement on	F	F	F	F
R	0.055	0.051	0.049	0.062
wR	0.055	0.051	0.048	0.066
S	1.33	1.66	1.25	1.50
No. of reflections used in refinement	1468	1187	1592	1984
No. of parameters used	163	234	234	163
H-atom treatment	H atoms riding with C—H = 0.96, N—H 0.90 Å	H atoms riding with C—H = 0.96, N—H 0.90 Å	H atoms riding with C—H = 0.96, N—H 0.90 Å	H atoms riding with C—H = 0.96, N—H 0.90 Å
Weighting scheme	$w = 1/[\sigma^2(F_o) + 0.0005\|F_o\|^2]$	$w = 1/[\sigma^2(F_o) + 0.0002\|F_o\|^2]$	$w = 1/[\sigma^2(F_o) + 0.0004\|F_o\|^2]$	$w = 1/[\sigma^2(F_o) + 0.0005\|F_o\|^2]$
$(\Delta/\sigma)_{\max}$	0.002	0.061	0.012	0.001
$\Delta\rho_{\max}$ (e Å^{-3})	0.56	0.49	0.66	0.82
$\Delta\rho_{\min}$ (e Å^{-3})	−0.41	−0.42	−0.97	−0.94
Extinction method	None	$F_{\rm corr} = F_c(1 + 0.002 \times \chi F_c^2/\sin 2\theta)^{-1/4}$	$F_{\rm corr} = F_c(1 + 0.002 \times \chi F_c^2/\sin 2\theta)^{-1/4}$	None
Extinction parameter	-	$\chi = 4.4 \times 10^{-4}$	$\chi = 1.0 \times 10^{-3}$	-
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)	*International Tables for X-ray Crystallography* (1974, Vol. IV)

the hydrogen-bonding capability of selenourea and, at the same time, gather useful structural data for the N—H···Se hydrogen bond. As a natural extension of our current research program, we report the preparation and structural characterization of the following crystalline inclusion compounds of selenourea

$$(C_2H_5)_4N^+.Cl^-.2[(NH_2)_2CSe] \qquad (1)$$

$$(n\text{-}C_3H_7)_4N^+.Cl^-.3[(NH_2)_2CSe] \qquad (2)$$

$$(n\text{-}C_3H_7)_4N^+.Br^-.3[(NH_2)_2CSe] \qquad (3)$$

$$(n\text{-}C_3H_7)_4N^+.I^-.(NH_2)_2CSe. \qquad (4)$$

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$) *for (1)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Selenourea–chloride host lattice				
Se(1)	0.1140 (1)	0.0923 (1)	0.2921 (1)	0.061 (1)
C(1)	0.1755 (3)	0.2095 (3)	0.2343 (3)	0.053 (1)
N(1)	0.2226 (3)	0.1836 (3)	0.1761 (2)	0.073 (1)
N(2)	0.1758 (3)	0.3258 (3)	0.2514 (2)	0.063 (1)
Se(2)	−0.0624 (1)	0.1219 (1)	0.5836 (1)	0.078 (1)
C(2)	0.0303 (3)	0.2231 (3)	0.5256 (3)	0.049 (1)
N(3)	0.0307 (3)	0.3402 (3)	0.5328 (2)	0.071 (1)
N(4)	0.0914 (3)	0.1766 (3)	0.4737 (2)	0.064 (1)
Cl(1)	0.1583 (2)	0.4470 (2)	0.3999 (1)	0.086 (1)
Tetraethylammonium ion				
N(5)	0.1249 (3)	0.2620 (3)	0.8663 (3)	0.107 (1)
C(3)	0.0732 (3)	0.2548 (3)	0.7915 (3)	0.181 (1)
C(4)	0.1934 (3)	0.2654 (3)	0.7509 (3)	0.574 (1)
C(5)	0.2089 (3)	0.3744 (3)	0.8863 (3)	0.125 (1)
C(6)	0.1126 (3)	0.4828 (3)	0.8748 (3)	0.283 (1)
C(7)	−0.0055 (3)	0.2480 (3)	0.9005 (3)	0.235 (1)
C(8)	0.0193 (3)	0.2466 (3)	0.9775 (3)	0.273 (1)
C(9)	0.2355 (3)	0.1685 (3)	0.8883 (3)	0.279 (1)
C(10)	0.1737 (3)	0.0456 (3)	0.8746 (3)	0.490 (1)

The exponent of the isotropic temperature factor takes the form $-8\pi^2 U\sin^2\theta/\lambda^2$.

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$) *for (2) and (3)*

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
(i) $(n\text{-}C_3H_7)_4N^+.Cl^-.3[(NH_2)_2CSe]$ (2)				
Selenourea–chloride host lattice				
Se(1)	0.5780	0.4349 (2)	0.4744	0.061 (1)
C(1)	0.6443 (3)	0.4747 (3)	0.3933 (3)	0.046 (1)
N(1)	0.6181 (3)	0.4905 (3)	0.2715 (3)	0.045 (1)
N(2)	0.7218 (3)	0.4735 (3)	0.4535 (3)	0.058 (1)
Se(2)	0.4219 (1)	0.5652 (2)	0.0944 (1)	0.062 (1)
C(2)	0.3471 (3)	0.5358 (3)	0.1646 (3)	0.053 (1)
N(3)	0.2695 (3)	0.5376 (3)	0.1046 (3)	0.071 (1)
N(4)	0.3762 (3)	0.4961 (3)	0.2774 (3)	0.101 (1)
Se(3)	0.8141 (2)	0.4313 (2)	0.7720 (2)	0.102 (1)
C(3)	0.7739 (3)	0.3061 (3)	0.7793 (3)	0.090 (1)
N(5)	0.8124 (3)	0.2442 (3)	0.8694 (3)	0.110 (1)
N(6)	0.6988 (3)	0.2821 (3)	0.7108 (3)	0.076 (1)
Cl(1)	0.1853 (2)	0.4315 (3)	0.2954 (3)	0.028 (1)
Tetrapropylammonium ion				
N(7)	0.0019 (3)	0.2872 (3)	0.5248 (3)	0.057 (1)
C(4)	−0.0684 (3)	0.2162 (3)	0.5075 (3)	0.081 (1)
C(5)	−0.1487 (3)	0.2668 (3)	0.4941 (3)	0.074 (1)
C(6)	−0.2255 (3)	0.1978 (3)	0.4503 (3)	0.090 (1)
C(7)	0.0777 (3)	0.2251 (3)	0.5520 (3)	0.057 (1)
C(8)	0.1505 (3)	0.2773 (3)	0.5861 (3)	0.082 (1)
C(9)	0.2075 (3)	0.2055 (3)	0.5827 (3)	0.096 (1)
C(10)	0.0187 (3)	0.3473 (3)	0.6468 (3)	0.043 (1)
C(11)	0.0374 (3)	0.2957 (3)	0.7660 (3)	0.070 (1)
C(12)	0.0643 (3)	0.3648 (3)	0.8817 (3)	0.104 (1)
C(13)	−0.0071 (3)	0.3620 (3)	0.4194 (3)	0.087 (1)
C(14)	−0.0219 (3)	0.3086 (3)	0.2934 (3)	0.124 (1)
C(15)	−0.0322 (3)	0.3776 (3)	0.1939 (3)	0.081 (1)
(ii) $(n\text{-}C_3H_7)_4N^+.Br^-.3[(NH_2)_2CSe]$ (3)				
Selenourea–bromide host lattice				
Se(1)	0.5780	0.4360 (2)	0.4744	0.057 (1)
C(1)	0.6457 (3)	0.4662 (3)	0.3956 (3)	0.041 (1)
N(1)	0.6195 (3)	0.4945 (3)	0.2779 (3)	0.068 (1)
N(2)	0.7224 (3)	0.4641 (4)	0.4620 (4)	0.093 (1)
Se(2)	0.4226 (1)	0.5648 (2)	0.0936 (1)	0.070 (1)
C(2)	0.3550 (3)	0.5304 (4)	0.1714 (3)	0.076 (1)
N(3)	0.2775 (3)	0.5344 (4)	0.1161 (3)	0.062 (1)
N(4)	0.3846 (3)	0.5048 (4)	0.2905 (3)	0.094 (1)
Se(3)	0.8165 (2)	0.4369 (2)	0.7754 (2)	0.072 (1)
C(3)	0.7770 (3)	0.3120 (3)	0.7813 (4)	0.066 (1)
N(5)	0.8192 (3)	0.2450 (3)	0.8607 (4)	0.080 (1)
N(6)	0.7050 (3)	0.2825 (3)	0.7080 (4)	0.070 (1)
Br(1)	0.1812 (2)	0.4397 (2)	0.2900 (3)	0.083 (1)
Tetrapropylammonium ion				
N(7)	−0.0045 (4)	0.2866 (3)	0.5250 (4)	0.057 (1)
C(4)	−0.0707 (3)	0.2166 (4)	0.5213 (4)	0.064 (1)
C(5)	−0.1485 (3)	0.2700 (4)	0.5043 (4)	0.055 (1)
C(6)	−0.2228 (3)	0.2031 (4)	0.4606 (4)	0.089 (1)
C(7)	0.0695 (3)	0.2234 (4)	0.5616 (4)	0.085 (1)
C(8)	0.1480 (3)	0.2765 (4)	0.6009 (4)	0.088 (1)
C(9)	0.2019 (4)	0.1991 (4)	0.5918 (4)	0.116 (1)
C(10)	0.0183 (4)	0.3520 (4)	0.6433 (4)	0.078 (1)
C(11)	0.0272 (4)	0.3052 (4)	0.7699 (4)	0.073 (1)
C(12)	0.0596 (4)	0.3717 (4)	0.8818 (4)	0.112 (1)
C(13)	−0.0116 (3)	0.3521 (4)	0.4197 (4)	0.048 (1)
C(14)	−0.0354 (4)	0.2923 (4)	0.3022 (4)	0.126 (1)
C(15)	−0.0397 (3)	0.3661 (4)	0.1989 (4)	0.074 (1)

The exponent of the isotropic temperature factor takes the form $-8\pi^2 U\sin^2\theta/\lambda^2$.

2. Experimental

All reactions were performed under a nitrogen atmosphere with the use of standard Schlenk techniques. Tetraethylammonium chloride, tetra-*n*-propylammonium bromide and iodide were obtained from Eastman Kodak. Each quaternary ammonium salt and selenourea were mixed in a molar ratio of 1:2 and then an appropriate quantity of ethanol was added and warmed to ~313 K to dissolve the solid. After stirring for ~30 min, the solution was cooled to 283 K. Colorless crystals appeared in the form of small blocks for (1) and thin plates for (2), (3) and (4). All complexes are air-sensitive and were sealed in Lindemann glass capillaries for X-ray structure determination.

Information concerning crystallographic data and structure refinement of the three compounds is summarized in Table 1. Intensities were collected in the variable ω-scan technique (Sparks, 1976) on a Siemens P4 diffractometer using Mo $K\alpha$ radiation (λ = 0.71073 Å) at 291 K. The raw data were processed with a learnt-profile procedure (Kopfmann & Huber, 1968) and an empirical absorption correction based on ψ-scan data was also applied.

All calculations were performed on a PC 486 computer with the *SHELXTL-Plus* program package (Sheldrick, 1982). All non-H atoms were located by direct methods and all were assigned anisotropic thermal parameters. The amido, methylene and methyl H atoms were generated geometrically (C—H and N—H distance fixed at 0.96 and 0.90 Å, respectively) and allowed to ride on their respective parent atoms. All H atoms were assigned appropriate isotropic temperature factors and included in the structure-factor calculations. Analytical expressions of atomic scattering factors were employed and anomalous dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1974, Vol. IV). The refinement of the coordinates and

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for (4)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Selenourea–iodide host lattice				
Se(1)	0.2454 (1)	−0.0535 (1)	0.5002 (1)	0.064 (1)
C(1)	0.2504 (2)	0.0719 (2)	0.4781 (2)	0.046 (1)
N(1)	0.3746 (2)	0.1130 (2)	0.4589 (2)	0.058 (1)
N(2)	0.1283 (2)	0.1225 (2)	0.4800 (2)	0.064 (1)
I(1)	0.2839 (1)	0.3533 (1)	0.4524 (1)	0.077 (1)
Tetrapropylammonium ion				
N(3)	0.2092 (2)	0.1705 (2)	0.1603 (2)	0.041 (1)
C(2)	0.1098 (2)	0.2520 (2)	0.1581 (2)	0.153 (1)
C(3)	0.0374 (2)	0.2966 (2)	0.2128 (2)	0.122 (1)
C(4)	−0.0360 (2)	0.3821 (2)	0.2013 (2)	0.096 (1)
C(5)	0.1396 (2)	0.0971 (2)	0.2079 (2)	0.132 (1)
C(6)	0.0203 (2)	0.0569 (2)	0.2137 (2)	0.201 (1)
C(7)	−0.0375 (2)	−0.0131 (2)	0.2633 (2)	0.096 (1)
C(8)	0.2289 (2)	0.1389 (2)	0.0713 (2)	0.128 (1)
C(9)	0.3010 (2)	0.1661 (2)	0.0095 (2)	0.153 (1)
C(10)	0.3070 (2)	0.1337 (2)	−0.0773 (2)	0.111 (1)
C(11)	0.3576 (2)	0.1940 (2)	0.2010 (2)	0.163 (1)
C(12)	0.4854 (2)	0.1649 (2)	0.2078 (2)	0.175 (1)
C(13)	0.6207 (2)	0.1895 (2)	0.2479 (2)	0.147 (1)

anisotropic thermal parameters of the non-H atoms was carried out by the full-matrix least-squares method and the final *R* indices and other parameters are listed in Table 1.

3. Results and discussion

The final positional and equivalent isotropic thermal parameters of (1), (2), (3) and (4) are listed in Tables 2, 3 and 4 respectively.*

3.1. *Crystal structure of $(C_2H_5)_4N^+.Cl^-.2[(NH_2)_2CSe]$ (1)*

In (1) the cations are separated by selenourea–chloride puckered layers to generate a sandwich-like packing mode and the layer structure may be conveniently described with reference to the hydrogen-bonding scheme shown in Fig. 1 and Table 5. An independent selenourea molecule composed of atoms C(1), Se(1), N(1) and N(2) is repeated by a 2_1 screw axis and pairs of resulting molecules are interconnected by a single N—H···Se hydrogen bond of length N(2^i)···Se(1) = 3.629 (6) Å, to generate an infinite chain. The value of the torsion angle between two adjacent selenourea molecules, C(1^i)—N(2^i)···Se(1)—C(1) = −173.0 (4)°, indicates that this chain is almost planar. The second

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* Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: HR0033). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

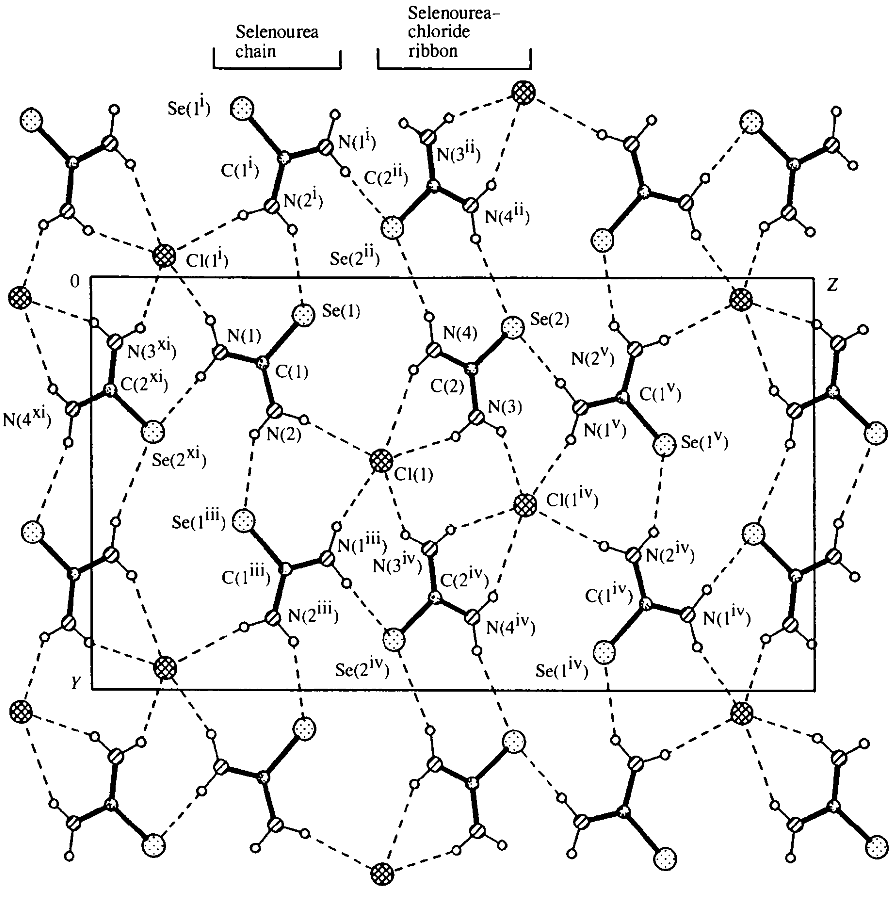

Fig. 1. Projection drawing of the hydrogen-bonded layer in $(C_2H_5)_4N^+.Cl^-.2[(NH_2)_2CSe]$ (1) formed by the crosslinkage of selenourea chains and selenourea-chloride ribbons. The atom labels correspond to those given in Tables 2 and 5. Dashed lines represent hydrogen bonds and atom types are distinguished by size and shading.

Table 5. *Selected bond distances (Å), bond angles (°) and torsion angles (°) in the selenourea–halide inclusion complexes*

$(C_2H_5)_4N^+.Cl^-.2[(NH_2)_2CSe]$ (1)			
(i) Selenourea molecules			
Se(1)—C(1)	1.849 (4)	C(1)—N(1)	1.300 (7)
C(1)—N(2)	1.328 (5)	Se(2)—C(2)	1.858 (4)
C(2)—N(3)	1.300 (5)	C(2)—N(4)	1.319 (6)
Se(1)—C(1)—N(1)	122.8 (3)	Se(1)—C(1)—N(2)	120.6 (4)
N(1)—C(1)—N(2)	116.6 (4)	Se(2)—C(2)—N(3)	121.7 (4)
Se(2)—C(2)—N(4)	119.8 (3)	N(3)—C(2)—N(4)	118.5 (4)
(ii) Hydrogen bonding			
N(2^{i})···Se(1)	3.629	N(1^{v})···Se(2)	3.513
N(4^{ii})···Se(2)	3.483	N(1^{iii})···Cl(1)	3.248
N(2)···Cl(1)	3.249	N(4)···Cl(1)	3.405
N(3)···Cl(1)	3.205	N(3^{iv})···Cl(1)	3.251
N(2^{i})···Se(1)—C(1)	103.0	N(1^{v})···Se(2)—C(2)	104.9
N(4^{ii})···Se(2)—C(2)	112.8	N(1^{v})···Se(2)···N(4^{ii})	136.5
N(1^{iii})···Cl(1)···N(2)	81.9	N(2)···Cl(1)···N(4)	93.5
N(4)···Cl(1)···N(3)	39.7	N(3)···Cl(1)···N(3^{iv})	71.6
N(3^{iv})···Cl(1)···N(1^{iii})	79.5		
C(1^{i})—N(2^{i})···Se(1)—C(1)	−173.0		
$(n\text{-}C_3H_7)_4N^+.Cl^-.3[(NH_2)_2CSe]$ (2)			
(i) Selenourea molecules			
Se(1)—C(1)	1.857 (5)	C(1)—N(1)	1.323 (5)
C(1)—N(2)	1.313 (6)	Se(2)—C(2)	1.863 (6)
C(2)—N(3)	1.313 (6)	C(2)—N(4)	1.326 (5)
Se(3)—C(3)	1.879 (5)	C(3)—N(5)	1.321 (5)
C(3)—N(6)	1.334 (6)		
Se(1)—C(1)—N(1)	122.8 (4)	Se(1)—C(1)—N(2)	119.6 (3)
N(1)—C(1)—N(2)	116.9 (5)	Se(2)—C(2)—N(3)	125.1 (3)
Se(2)—C(2)—N(4)	115.4 (4)	N(3)—C(2)—N(4)	118.7 (5)
Se(3)—C(3)—N(5)	121.6 (3)	Se(3)—C(3)—N(6)	121.7 (3)
N(5)—C(3)—N(6)	115.4 (5)		
(ii) Hydrogen bonding			
N(1^{vi})···Se(1)	3.386	N(4)···Se(1)	3.605
N(6)···Se(1)	3.487	N(1)···Se(2)	3.522
N(4^{vii})···Se(2)	3.537	N(5^{ix})···Se(2)	3.568
N(1^{vi})···Se(3)	3.703	N(2^{vi})···Se(3)	3.390
N(2)···Se(3)	3.471	N(3)···Cl(1)	3.434
N(3^{vi})···Cl(1)	3.342	N(4)···Cl(1)	3.647
N(5^{viii})···Cl(1)	3.219	N(6^{viii})···Cl(1)	3.127
N(1^{vi})···Se(1)···N(4)	110.6	N(4)···Se(1)···N(6)	145.5
N(1^{vi})···Se(1)···N(6)	63.6	N(1)···Se(2)···N(4^{vii})	109.1
N(4^{vii})···Se(2)···N(5^{ix})	64.0	N(1)···Se(2)···N(5^{ix})	141.6
N(1^{vi})···Se(3)···N(2^{vi})	36.6	N(2^{vi})···Se(3)···N(2)	115.9
N(1^{vi})···Se(3)···N(2)	82.4	N(3)···Cl(1)···N(3^{vi})	119.8
N(3^{vi})···Cl(1)···N(4)	88.1	N(4)···Cl(1)···N(5^{viii})	66.4
N(5^{viii})···Cl(1)···N(6^{viii})	41.4	N(3)···Cl(1)···N(4)	37.2
C(1)—N(1)···Se(2)—C(2)	−22.7	C(2)—N(4)···Se(1)—C(1)	2.6
C(1^{vi})—N(1^{vi})···Se(1)—C(1)	−78.5	C(2)—N(4)···Se(2^{vi})—C(2^{vi})	24.6
$(n\text{-}C_3H_7)_4N^+.Br^-.3[(NH_2)_2CSe]$ (3)			
(i) Selenourea molecules			
Se(1)—C(1)	1.845 (6)	C(1)—N(1)	1.319 (5)
C(1)—N(2)	1.319 (7)	Se(2)—C(2)	1.850 (6)
C(2)—N(3)	1.316 (7)	C(2)—N(4)	1.322 (5)
Se(3)—C(3)	1.882 (6)	C(3)—N(5)	1.324 (6)
C(3)—N(6)	1.330 (7)		
Se(1)—C(1)—N(1)	121.9 (4)	Se(1)—C(1)—N(2)	118.3 (3)
N(1)—C(1)—N(2)	119.6 (5)	Se(2)—C(2)—N(3)	123.4 (3)
Se(2)—C(2)—N(4)	119.5 (4)	N(3)—C(2)—N(4)	117.1 (5)
Se(3)—C(3)—N(5)	122.3 (4)	Se(3)—C(2)—N(6)	124.0 (3)
N(5)—C(3)—N(6)	113.7 (5)		

Table 5 (*cont.*)

(ii) Hydrogen bonding			
N(1^{vi})···Se(1)	3.436	N(4)···Se(1)	3.495
N(6)···Se(1)	3.523	N(1)···Se(2)	3.552
N(4^{vii})···Se(2)	3.444	N(5^{ix})···Se(2)	3.626
N(1^{vi})···Se(3)	3.741	N(2^{vi})···Se(3)	3.514
N(2)···Se(3)	3.391	N(3)···Br(1)	3.403
N(3^{vi})···Br(1)	3.522	N(4)···Br(1)	3.829
N(5^{viii})···Br(1)	3.461	N(6^{viii})···Br(1)	3.288
N(1^{vi})···Se(1)···N(4)	108.9	N(4)···Se(1)···N(6)	148.1
N(1^{vi})···Se(1)···N(6)	63.9	N(1)···Se(2)···N(4^{vii})	107.4
N(4^{vii})···Se(2)···N(5^{ix})	65.7	N(1)···Se(2)···N(5^{ix})	139.2
N(1^{vi})···Se(3)···N(2^{vi})	36.5	N(2^{vi})···Se(3)···N(2)	116.5
N(1^{vi})···Se(3)···N(2)	83.3	N(3)···Br(1)···N(3^{vi})	115.8
N(3^{vi})···Br(1)···N(4)	83.5	N(4)···Br(1)···N(5^{viii})	63.3
N(5^{viii})···Br(1)···N(6^{viii})	38.4	N(3)···Br(1)···N(4)	35.6
C(1)—N(1)···Se(2)—C(2)	−13.1	C(2)—N(4)···Se(1)—C(1)	13.4
C(1^{vi})—N(1^{vi})···Se(1)—C(1)	−18.6	C(2)—N(4)···Se(2^{vi})—C(2^{vi})	−30.5
$(n\text{-}C_3H_7)_4N^+.I^-.(NH_2)_2CSe$ (4)			
(i) Selenourea molecules			
Se(1)—C(1)	1.846 (3)	C(1)—N(1)	1.316 (3)
C(1)—N(2)	1.320 (3)		
Se(1)—C(1)—N(1)	121.2 (2)	Se(1)—C(1)—N(2)	120.6 (2)
N(1)—C(1)—N(2)	118.3 (3)		
(ii) Hydrogen bonding			
N(1^{x})···Se(1)	3.529	N(2^{ii})···Se(1)	3.534
N(1)···I(1)	3.567	N(2)···I(1)	3.652
N(1^{x})···Se(1)—C(1)	103.7	N(2^{ii})···Se(1)—C(1)	109.2
N(1^{x})···Se(1)···N(2^{ii})	145.8		
C(1^{x})—N(1^{x})···Se(1)—C(1)	−19.5	C(1)—N(2)···Se(1^{ii})—C(1^{ii})	7.2

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $-x, -y, 1-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-x, 1-y, 1-z$; (v) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $x, 1-y, \frac{1}{2}+z$; (vii) $x, 1-y, z-\frac{1}{2}$; (viii) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (ix) $x-\frac{1}{2}, \frac{1}{2}+y, z-1$; (x) $1-x, -y, 1-z$; (xi) $\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2}$. Standard deviations in hydrogen bond lengths and bond angles: (1), $\sigma(l) \simeq 0.006$ Å, $\sigma(\theta) \simeq 0.4°$; (2), $\sigma(l) \simeq 0.008$ Å, $\sigma(\theta) \simeq 0.4°$; (3), $\sigma(l) \simeq 0.007$ Å, $\sigma(\theta) \simeq 0.4°$; (4), $\sigma(l) \simeq 0.007$ Å, $\sigma(\theta) \simeq 0.5°$.

independent selenourea molecule [composed of C(2), Se(2), N(3) and N(4)] in the asymmetric unit links with a chloride ion through a pair of chelating N—H···Cl hydrogen bonds [N(3)···Cl(1) = 3.205 (6), N(4)···Cl(1) = 3.405 (6) Å] to generate a dimer, which together with its centrosymmetrically related partner constitute a (selenourea–chloride)$_2$ tetramer consolidated by a pair of N—H···Cl hydrogen bonds [N(3)···Cl(1^{iv}) = N(3^{iv})···Cl(1) = 3.251 (6) Å; Fig. 1]. This tetrameric unit is almost planar as the mean atomic deviation from the least-squares plane is 0.122 Å (including all non-H atoms in the tetramer). Linked alternately by pairs of N—H···Se hydrogen bonds between selenourea molecules arranged about inversion centers, these tetrameric units form a zigzag ribbon running parallel to the *b* axis. The selenourea–chloride ribbons and selenourea chains are alternately arranged and crosslinked by N—H···Cl and N—H···Se hydrogen bonds to form a puckered layer matching the (202) plane (Fig. 2).

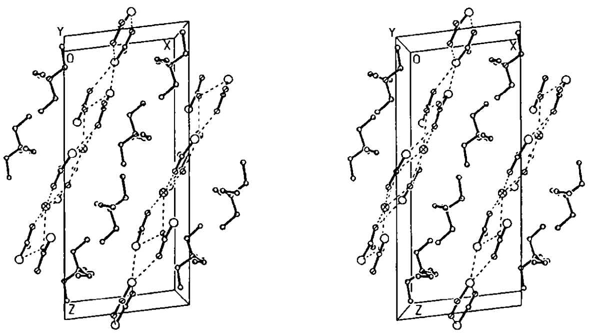

Fig. 2. Stereodrawing of the layer structure of (1). The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right, *b* towards the reader and *c* downwards. Dashed lines represent hydrogen bonds and atom types are distinguished by size and shading.

The tetrahedral $(C_2H_5)_4N^+$ cation is well ordered and almost attains its idealized 222 molecular symmetry. A stereodrawing of the crystal structure is illustrated in Fig. 2. It is seen that the cations are arranged in a layer corresponding to the (101) plane and are located in the space between the host layers.

3.2. *Crystal structure of* $(n\text{-}C_3H_7)_4N^+.Cl^-.3[(NH_2)_2CSe]$ *(2) and* $(n\text{-}C_3H_7)_4N^+.Br^-.3[(NH_2)_2CSe]$ *(3)*

Complexes (2) and (3) are virtually isomorphous with the same basic skeleton and only differ in the halide ions. The hydrogen-bonding scheme of (2) is shown in Fig. 3. Two independent selenourea molecules of an asymmetric unit are connected by a pair of N—H···Se hydrogen bonds in a shoulder-to-shoulder fashion to form a dimer, which is approximately planar, as shown by the C(1)—N(1)···Se(2)—C(2) torsion angles of −22.7° for (2) and −13.1° for (3). These selenourea dimers are interlinked laterally by additional N—H···Se hydrogen bonds and bridging chloride ions on one side, each *via* three N—H···X hydrogen bonds, with N(3$^{\rm vi}$)···Cl(1) = 3.342 (8), N(3)···Cl(1) = 3.434 (8) and N(4)···Cl(1) = 3.647 (8) Å for (2), and N(3$^{\rm vi}$)···Br(1) = 3.522 (8), N(3)···Br(1) = 3.403 (8) and N(4)···Br(1) = 3.829 (8) Å for (3), respectively. On the other side, the Se atom of the third independent selenourea molecule in the asymmetric unit bridges adjacent selenourea dimers *via* three N—H···Se hydrogen bonds in the same manner as a halide ion. Thus, an anionic double ribbon running parallel to the [001] direction is generated (Fig. 3). For this buckled double ribbon the deviation of its molecular components from co-planarity can be judged by the angle between the least-square planes of a pair of adjacent dimers, which is 44.1 (4)° for (2) and 42.9 (4)° for (3). The double ribbons are concentrated in layers that match the (020) family of planes. The N atoms of the third bridging selenourea molecule form a pair of N—H···X hydrogen bonds to a halide ion in chelating fashion [N(5$^{\rm viii}$)···Cl(1) = 3.219 (8), N(6$^{\rm viii}$)···Cl(1) = 3.127 (8), N(5$^{\rm viii}$)···Br(1) = 3.461 (7) and N(6$^{\rm viii}$)···Br(1) = 3.288 (7) Å]. Since the Se atom of this selenourea molecule also forms three N—H···Se hydrogen bonds with two selenourea molecules in the ribbon that are related by an n glide, it plays a very similar and complementry role as a halide ion. Thus, the wide selenourea–halide double ribbons are crosslinked by bridging selenourea molecules to generate a three-dimensional network containing an open-channel system running in the [101] direction (Fig. 4).

The tetra-n-propylammonium cation almost attains idealized $\bar{4}2m$ molecular symmetry and has normal molecular dimensions. The stereoview of the crystal structure clearly shows that a stacked column of cations is accommodated within each channel (Fig. 4).

3.3. *Crystal structure of* $(n\text{-}C_3H_7)_4N^+.I^-.(NH_2)_2CSe$ *(4)*

Compound (4) is isomorphous with its thio analog (n-$C_3H_7)_4N^+.I^-.(NH_2)_2CS$ (4*a*) [$P2_1/n$, a = 8.858 (2), b = 14.358 (3), c = 15.379 (3) Å, β = 93.88 (1)°, Z = 4], which has been reported in our previous study on a series of inclusion complexes of thiourea with peralkylated

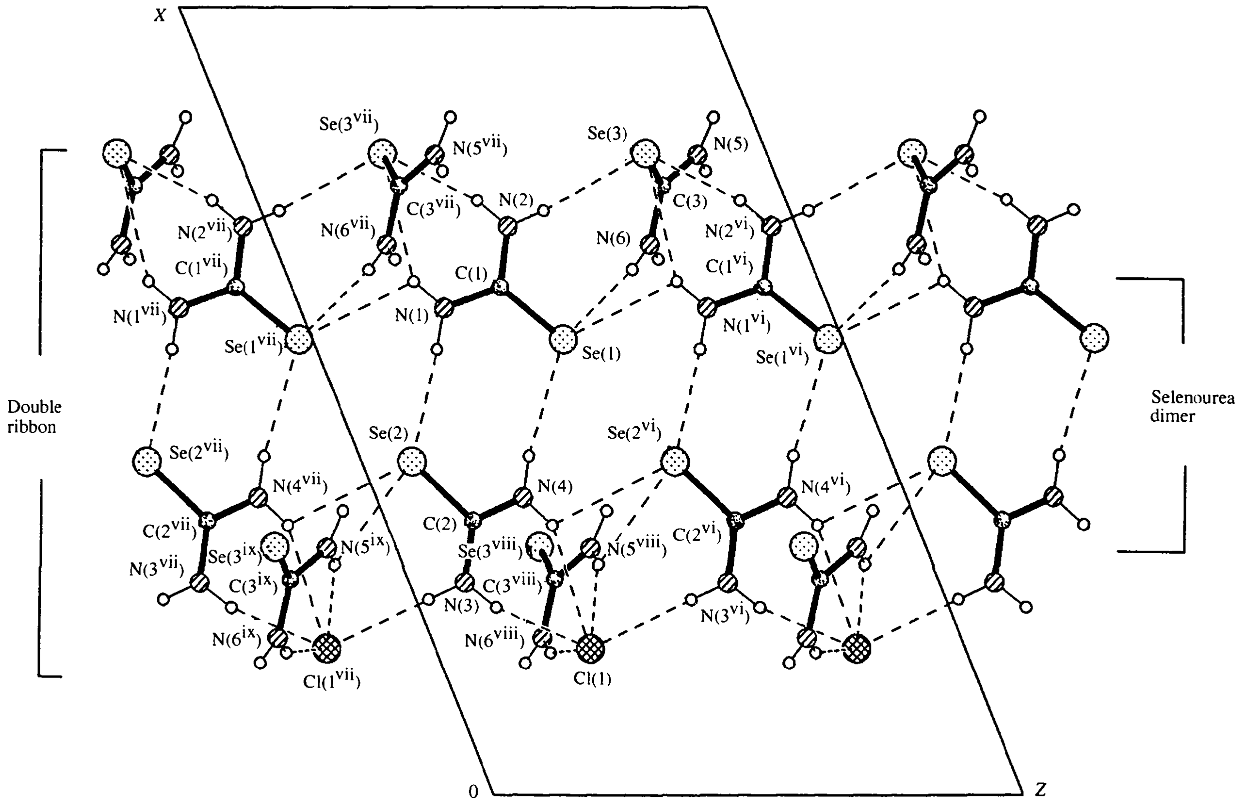

Fig. 3. Selenourea–chloride double ribbon in $(n\text{-}C_3H_7)_4N^+.Cl^-.3[(NH_2)_2CSe]$ (2), which is isostructural to the selenourea–bromide double ribbon in $(n\text{-}C_3H_7)_4N^+.Br^-.3[(NH_2)_2CSe]$ (3). The atom labels correspond to those given in Tables 3 and 5. Dashed lines represent hydrogen bonds.

ammonium halide salts (Mak, 1990). Changing the host molecule from thiourea to selenourea merely results in a small increase of the unit-cell dimensions.

Fig. 5 shows the crystal structure of (4), which is built of a packing of the selenourea–iodide composite ribbons and the tetra-*n*-propylammonium ions. The atom labeling and hydrogen-bonding interactions are shown in Fig. 6. The selenourea molecules are linked by N—H···Se hydrogen bonds [$N(1^{x})\cdots Se(1) = 3.529\,(7)$ and $N(2^{ii})\cdots Se(1) = 3.534\,(7)$ Å] in the shoulder-to-shoulder manner to form a zigzag ribbon running parallel to the *a* axis, with the iodide ions attached to it on both sides *via* N—H···I interactions [N···I = 3.567 (7) and 3.652 (7) Å].

3.4. *General structural features and selenourea molecular dimensions*

The present series of selenourea–quaternary ammonium halide complexes exhibit different types of anionic lattices, depending on the stoichiometric ratio of selenourea-to-halide ion. Compound (1) (2:1) has a layer-type host structure, isomorphous compounds (2) and (3) (3:1) feature an open-channel system constructed from double ribbons, whereas (4) (1:1) is isostructural with its thiourea analog and characterized by a composite ribbon composed of a zigzag arrangement of selenourea molecules with iodide ions attached to both sides.

The selenourea molecule has the expected planar conformation in all four complexes, except the bridging selenourea molecules in (2) and (3) [Se(3)—C(3) = 1.879 (5) and 1.882 (6) Å in (2) and (3), respectively], with measured dimensions [averaged values C—Se = 1.852 (8), C—N = 1.318 (8) Å and Se—C—N = 120.9 (5), N—C—N = 117.9 (5)°] that are consistent within the series but differ from those reported for the pure compound [1.86 (8)–1.94 (10), 1.33 (9)–1.44 (9) Å and 114 (6)–131 (8), 108 (6)–127 (6)°, for nine selenourea molecules (Rutherford & Calvo, 1969)] and the channel-type adamantane adduct of selenourea [1.91 (1), 1.30 (1) Å, 118 (1), 124 (2)° (Gopal, Robertson & Rutherford, 1989)]. The latter two sets of molecular dimensions for the selenourea molecule are believed to be unreliable, as the crystal structure analysis of neat selenourea was based on film data and the precision of the selenourea–adamantane adduct structure is severely affected by disorder of the adamantane guest molecule. The present structural parameters are in good agreement with those reported for the selenourea molecule in its crystalline adducts [$\{(NH_2)_2CSe\}_2SeC(NH_2)_2]SO_4.(NH_2)_2CSe.2H_2O$ [1.867 (4), 1.315 (6) Å, 120.6 (4), 118.8 (4)° (Hauge, 1979)] and $Co(acac)_3.2[(NH_2)_2CSe]$ [1.853 (5), 1.32 (1) Å, 120.8 (3), 118.3 (4)° (Wright & Meyers, 1980)].

The measured N···Se distances [ranging from 3.386 (8) to 3.741 (8) Å, with an average value of 3.527 (7) Å] for (1)–(4) are comparable to those found in the selenourea–adamantane inclusion complex, 3.51 (2) and 3.65 (2) Å, for N—H···Se hydrogen bonds between

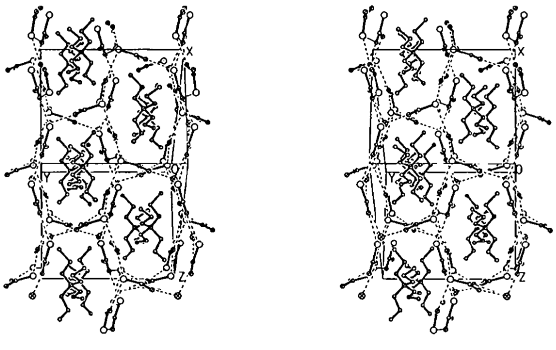

Fig. 4. Stereodrawing of the crystal structure of (2) [or (3)] showing the accommodation of a single column of $(n\text{-}C_3H_7)_4N^+$ ions in a channel running parallel to the [101] direction. The host structure is built from selenourea–halide double ribbons and bridging selenourea molecules. Note that the double ribbons lie close to the (020) planes and are crosslinked by the bridging selenourea molecules. Dashed lines represent hydrogen bonds and atom types are distinguished by size and shading.

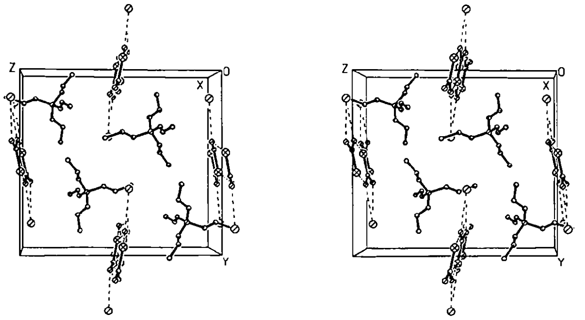

Fig. 5. Stereodrawing of the structure of $(n\text{-}C_3H_7)_4N^+.I^-.(NH_2)_2CSe$ (4). The origin of the unit cell lies at the upper right corner, with *a* pointing backwards from the reader, *b* downwards and *c* from right to left. Dashed lines represent hydrogen bonds and atom types are distinguished by size and shading.

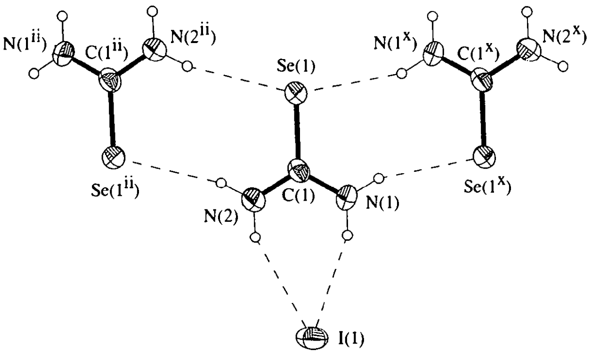

Fig. 6. Perspective view of a portion of the selenourea–iodide composite ribbon in (4). The atom labels correspond to those given in Tables 4 and 5. Dashed lines represent hydrogen bonds.

Table 6. *The N—H···X and O—H···X hydrogen bonds (Å) in some urea/thiourea/water-halide host lattices*

	Compound	Minimum	Maximum	Number of hydrogen bonds/X$^-$	Reference
N—H···*X*	In urea-halide host lattices				
	$(C_2H_5)_4N^+.Cl^-.2[(NH_2)_2CO]$	3.254 (5)	3.368 (5)	4	Li & Mak (1997*e*)
	$(C_2H_5)_4P^+.Cl^-.2[(NH_2)_2CO]$	3.331 (9)	3.402 (9)	4	Li & Mak (1997*e*)
	$(n\text{-}C_3H_7)_4N^+.Cl^-.2[(NH_2)_2CO]$	3.317 (7)	3.366 (7)	4	Li & Mak (1997*d*)
	$(n\text{-}C_3H_7)_4N^+.Cl^-.3[(NH_2)_2CO]$	3.303 (6)	3.424 (6)	6	Li & Mak (1997*d*)
	In urea-halide-water host lattices				
	$2(n\text{-}C_3H_7)_4N^+.F^-.7[(NH_2)_2CO].3H_2O$	2.737 (8)	3.003 (8)	3, F(1)	Li & Mak (1996*f*)
		2.805 (8)	2.914 (8)	2, F(2)	
	$(C_2H_5)_4N^+.Cl^-.(NH_2)_2CO.2H_2O$	3.379 (5)		1	Mak & McMullan (1988)
	$(C_2H_5)_4N^+.Br^-.(NH_2)_2CO.2H_2O$	3.53 (2)		1	Mak & McMullan (1988)
	$(n\text{-}C_3H_7)_4N^+.Br^-.3[(NH_2)_2CO].H_2O$	3.491 (3)		1	Li & Mak (1997*d*)
	$(n\text{-}C_3H_7)_4N^+.I^-.3[(NH_2)_2CO].H_2O$	3.722 (4)		1	Li & Mak (1997*d*)
	In thiourea-halide host lattices				
	$(n\text{-}C_4H_9)_4N^+.F^-.3[(NH_2)_2CS]$	2.819 (5)	2.994 (7)	6	Mak (1990)
	$(n\text{-}C_4H_9)_3N(CH_3)^+.Cl^-.2[(NH_2)_2CS]$	3.252 (3)	3.291 (3)	4	Mak (1990)
	$(n\text{-}C_4H_9)_4N^+.Cl^-.2[(NH_2)_2CS]$	3.206 (7)	3.321 (7)	4	Li & Mak (1996*b*)
	$(n\text{-}C_4H_9)_3N(CH_3)^+.Br^-.2[(NH_2)_2CS]$	3.353 (6)	3.459 (6)	4	Mak (1990)
	$(n\text{-}C_3H_7)_4N^+.I^-.(NH_2)_2CS$	3.564 (5)	3.680 (5)	2	Mak (1990)
O—H···*X*	In water-halide host lattices				
	$4(C_2H_5)_4N^+.F^-.11H_2O$	2.59 (1)	2.76 (1)	4, F(1)	Mak (1985)
		2.63 (1)	2.72 (1)	4, F(2)	
		2.65 (1)	2.85 (1)	4, F(3)	
		2.61 (1)	2.70 (1)	4, F(4)	
	$(C_2H_5)_4N^+.Cl^-.4H_2O$	3.177 (7)	3.244 (7)	4	Mak, Bruins Slot & Beurskens (1986)
	In urea-halide-water host lattices				
	$2(n\text{-}C_3H_7)_4N^+.F^-.7[(NH_2)_2CO].3H_2O$	2.620 (8)	2.716 (8)	2, F(1)	Li & Mak (1997*d*)
		2.471 (8)	2.705 (8)	2, F(2)	
	$(C_2H_5)_4N^+.Cl^-.(NH_2)_2CO.2H_2O$	3.178 (5)	3.223 (5)	3	Mak & McMullan (1988)
	$(C_2H_5)_4N^+.Br^-.(NH_2)_2CO.2H_2O$	3.16 (2)	3.36 (2)	3	Mak & McMullan (1988)
	$(n\text{-}C_3H_7)_4N^+.Br^-.3[(NH_2)_2CO].H_2O$	3.361 (3)	3.390 (3)	2	Li & Mak (1997*d*)
	$(n\text{-}C_3H_7)_4N^+.I^-.3[(NH_2)_2CO].H_2O$	3.570 (4)	3.672 (4)	2	Li & Mak (1997*d*)

chains and within chains, respectively (Gopal, Robertson & Rutherford, 1989). The weakest N—H···Se hydrogen bond in the present series of inclusion compounds occurs in the singly hydrogen-bonded selenourea chain in (1) and the bridging selenourea molecule between double ribbons in (2) and (3). There is a distinct difference between the average value of the present N···Se distances and mean N···S bond length (3.472 Å with standard deviation 0.080) obtained from 111 measured N—H···S hydrogen bonds of 23 thiourea–anion host lattices (Li, 1996). The unusually long [3.397 (3), 3.522 (8) and 3.683 (6) Å] N—H···S distances in pure thiourea arise because each molecule forms a total of six hydrogen bonds (Mullen, Heger & Treutmann, 1978).

It is noted that the N—H···*X* hydrogen bonds in the present series of selenourea–halide complexes play an important role to consolidate the host lattices. In compounds (1), (2) and (3) there are five N—H···*X* hydrogen bonds per chloride or bromide ion and the ten measured N—H···Cl distances range from 3.127 (8) to 3.647 (8) Å, with an average value of 3.304 (8) Å, and five N—H···Br distances from 3.288 (7) to 3.829 (7) Å, with an average value of 3.502 (7) Å. The respective averages lie within the range of N—H···Cl [3.206 (7)–3.393 (9) Å] and N—H···Br [3.353 (9)–3.53 (2) Å] bond lengths compiled from 29 N—H···Cl hydrogen bonds in eight complexes and six N—H···Br hydrogen bonds in three complexes possessing urea or thiourea–halide host lattices (Table 6). In inclusion compound (4) the measured chelating N—H···I hydrogen bonds [N···I 3.567 (8) and 3.652 (8) Å, with an average value of 3.608 (8) Å] and the N···I···N angle [36.8 (6)°] are in good agreement with those [3.622 (5) Å and 36.4 (3)°] determined for the related thiourea inclusion compound $(n\text{-}C_3H_7)_4N^+.I^-.(NH_2)_2CS$ (Mak, 1990).

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