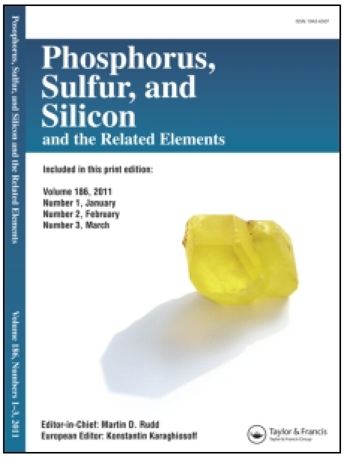

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SYNTHESES AND CRYSTAL STRUCTURES OF Di-μ-CHLORO-BIS [DITHIOCYANATOSELENATE(II)] AND Di-μ-BROMO-BIS [DITHIOCYANATOSELENATE(II)] SALTS

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The compounds were prepared by oxidation of elemental selenium with halogen and addition of $[C_6H_5(CH_3)_3N]SCN$ or $[(CH_3)_3NH]SCN$. The crystal structures have been determined by X-ray methods. $[C_6H_5(CH_3)_3N]_2[Se_2(\mu\text{-}Cl)_2(SCN)_4]$ (**1**) and $[C_6H_5(CH_3)_3N]_2[Se_2(\mu\text{-}Br)_2(SCN)_4]$ (**2**) are isotypic, and so are $[(CH_3)_3NH]_2[Se_2(\mu\text{-}Cl)_2(SCN)_4]$ (**3**) and $[(CH_3)_3NH]_2[Se_2(\mu\text{-}Br)_2(SCN)_4]$ (**4**) The anions are *cis*-$SeX_2(SCN)_2$ squares (X = Cl or Br) dimerised by the halogen atoms. The terminal bonds, Se-S, are in the narrow range 2.252(1) – 2.295(2) Å whereas the bridging bonds are in the wider range; Se-Cl = 2.885(1) – 3.041(1) Å and Se-Br = 2.971(1) – 3.117(1) Å. In the structures of the isotypic pair **3** and **4** there are N-H···X hydrogen bonds between the $(CH_3)_3NH^+$cations and the halogen atoms, N···Cl = 3.114(3) Å and N···Br = 3.270(3) Å. The bridging bonds of these compounds are increased by an average of 0.087 Å compared to the corresponding bonds of the isotypic pair **1**and **2**.

Keywords: Selenium(II) complexes; N-H···X hydrogen bonds; asymmetric di-μ-halo complexes; crystal structures

INTRODUCTION

Dinuclear halo- or pseudohaloselenates(II) consist of two SeX_4 squares sharing one edge in a planar Se_2X_6 structure. The first known structures were of the pseudohalides selenocyanate and thiocyanate[1] and later a

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number of structures of chlorides and bromides have been published.[2–7] In one case two of the terminal Br atoms in $Se_2Br_6^{2-}$ were successfully replaced by SCN groups.[8] We report here the syntheses and crystal structures of four complexes where all terminal Br or Cl atoms are replaced by SCN groups, $[C_6H_5(CH_3)_3N]_2[Se_2(\mu\text{-}Cl)_2(SCN)_4]$ (**1**), $[C_6H_5(CH_3)_3N]_2[Se_2(\mu\text{-}Br)_2(SCN)_4]$ (**2**), $[(CH_3)_3NH]_2[Se_2(\mu\text{-}Cl)_2(SCN)_4]$ (**3**) and $[(CH_3)_3NH]_2[Se_2(\mu\text{-}Br)_2(SCN)_4]$ (**4**).

SYNTESES

The complexes were prepared by oxidation of selenium with halogen followed by addition of thiocyanate. Using equimolar amounts of selenium and halogen the first reaction may be summarised:

$$\mathbf{Se + X_2 = SeX_2} \qquad (1)$$

The reaction, however, leads to equilibrium between compounds where selenium has valences 0,1, 2 and 4. By addition of thiocyanate the solution, in addition to selenium in four oxidation states, contains two different possible ligands. With the known tendency of selenium to form monomer, dimer, oligomer and polymer halogen complexes it is obvious that this will create a complicated equilibrium between many different species, some in minute amounts and some as main components. Without knowledge of equilibrium constants and solubility products one has to use the method of trial and error to find a way to prepare a wanted compound. To prepare the complexes **1** – **4** we used different solvents and different temperatures, but in all cases the molar amount of thiocyanate was twice the molar amount of selenium:

$$\mathbf{2SeX_2 + 4SCN^- = [Se_2X_2(SCN)_4]^{2-} + 2X^-} \qquad (2)$$

As an illustration of the complexity one example will be mentioned. The amount of bromine was reduced by 1/3 with the intention of getting a complex with less Br^- and more SCN^- ligands, but one of the isolated products was characterised as $[C_6H_5(CH_3)_3N][SeBr_4]$ (**5**).

Except for **1**, which had to be protected by argon, the compounds are stable in air for a short period of time.

RESULTS AND DISCUSSION

The present compounds are prepared by reacting SeX_2 (X = Cl or Br) with SCN^-. Crystals of SeX_2 have not been isolated, but the structures are known from electron diffraction studies.[12] The bond lengths found in these studies and the crystal structures of the corresponding pseudo-halides $Se(SeCN)_2$ and $Se(SCN)_2$[13] are close to the sums of the covalent radii and the bond angles are in the range 100–105°. When thiocyanate is added to the SeX_2solution it will react through linear attacks *trans* to the halogen atoms. Two linear three-centre four-electron (3*c*-4*e*) bonding systems, S-Se-X, at approximately right angles are established. The resulting four-coordinated anion complex $[SeX_2(SCN)_2]^{2-}$ has not been isolated whereas the corresponding halides $[SeX_4]^{2-}$ are well known for X = Cl or Br.[14] Since thiocyanate is a better nucleophile towards selenium than halide, the strong *trans* influence of thiocyanate may expel some of the halide ions and thereby increase the possibility of forming the dimer anions, $[Se_2(\mu\text{-}X)_2(SCN)_4]^{2-}$. The anions $[SeX_2(SCN)_2]^{2-}$ and $[Se_2(\mu\text{-}X)_2(SCN)_4]^{2-}$ may be regarded as intermediates in the S_N2 reaction between $SeX_2$and SCN^- where the final product would be $Se(SCN)_2$.

In compounds **1** – **4** the anions consist of two selenium atoms, each surrounded by two sulphur atoms and two halogen atoms in a nearly square-planar arrangement. A centre of symmetry relates the halogen atoms, which form bridges between the two selenium atoms. The planes through the selenium and halogen atoms are exact by symmetry and the maximum deviation of a sulphur atom from the planes are in the range 0.1002(18) – 0.2274(12) Å. The two linear S-C-N groups of the same selenium atom are rotated to the same side of the selenium coordination plane.

Cell dimensions, space groups and atomic coordinates show that the chlorine and bromine compounds of the same cations have isotypic crystal structures. The isotypic pairs are **1** and **2**, and **3** and **4**. Views of the two chlorine compounds with numbering of atoms, which is identical for the isotypic bromine compounds, are shown in Figs. 1 and 2. Bond lengths and angles of the anions are listed in Table II. Selected dimensions in structures of $[Se_2(\mu\text{-}SCN)_2(SCN)_4]^{2-}$, $[Se_2(\mu\text{-}Cl)_2Cl_4]^{2-}$, $[Se_2(\mu\text{-}Br)_2Br_4]^{2-}$ and $[Se_2(\mu\text{-}Br)_2Br_2(SCN)_2]^{2-}$ ions are listed together with those of the present structures in Table III.

The terminal bonds to sulphur are only 0.06–0.11 Å longer than the covalent bond,[15] whereas the bridging bonds to halogen are in the range 0.67–

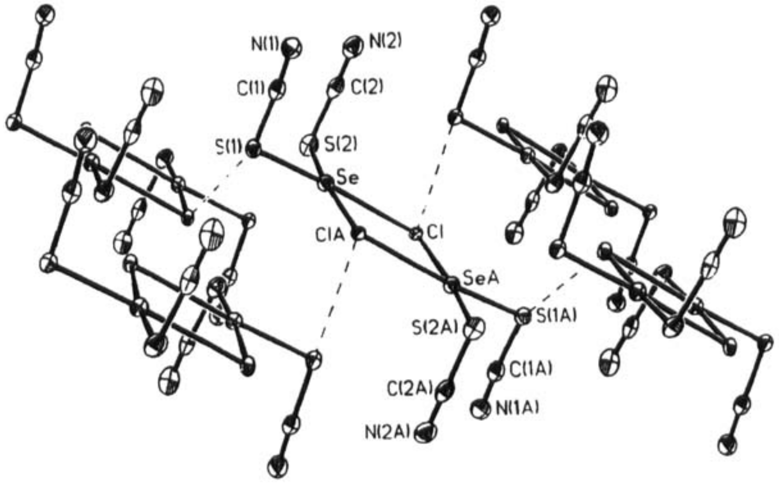

FIGURE 1 A view of the anion-network of $[C_6H_5(CH_3)_3N]_2[Se_2(\mu\text{-}Cl)_2(SCN)_4]$ (**1**) with numbering scheme

0.89 Å longer than the covalent bonds.[15,16] When a SeX_4^{2-} ion is dimerised through Se-X-Se bridges, the length of the bridging bonds will increase compared with the monomer ion, and the length of the terminal bonds will decrease to nearly the same extent. In the present structures the terminal bonds are to thiocyanate, which has larger *trans* influence or nucleophilicity than halides, and this will increase the asymmetry. Furthermore, in all four structures there are short contacts to the bridging atoms from adjacent ions and this will withdraw electrons from these atoms and thereby lower their *trans* influence and so increase the asymmetry.

In the isotypic pair **1** and **2** the shortest interionic contacts are between the bridging halogen atoms and S(1) with distances Cl···S(1) = 3.375(1) Å and Br···S(1) = 3.417(2) Å. The distances are considerable shorter than the sums of the der Waals radii, 3.65 and 3.80 Å, respectively.[16] Through these contacts the anions are polymerised since each anion is bonded to four other anions as illustrated in Fig. 1. The shortest distances between anions and cations are Cl···C(33) = 3.684(4) Å and Br···C(33) = 3.748(7) Å, and are thought to be without influence on the bonding system of the anions. In the other isotypic pair, **3** and **4**, the shortest distances between anions are considerable longer; Cl···S(1) = 3.684(1) Å and

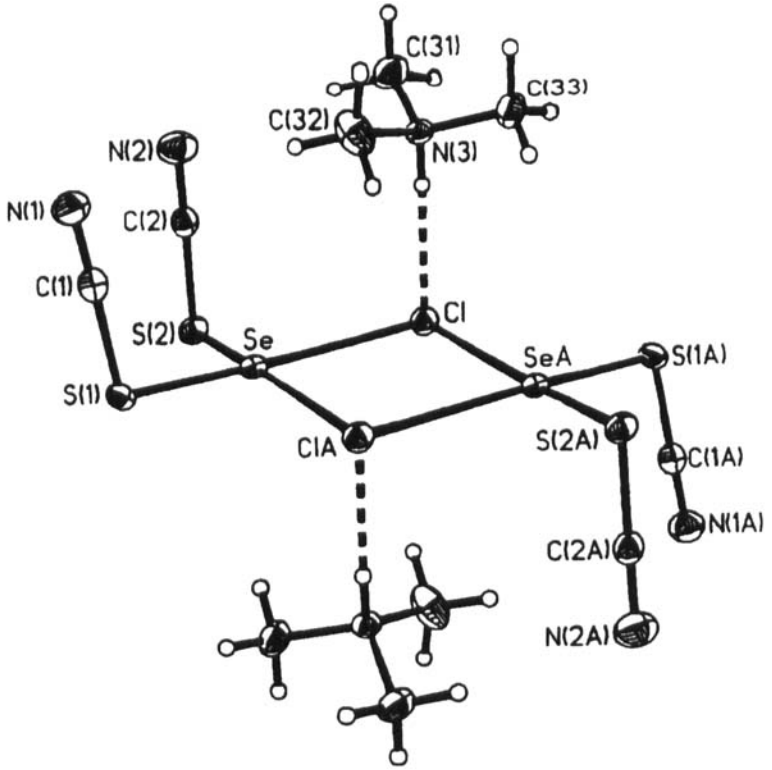

FIGURE 2 A view of $[(CH_3)_3NH]_2[Se_2(\mu\text{-}Cl)_2(SCN)_4]$ (3) with numbering scheme

Br···S(1) = 3.626(1) Å. In these structures, however, there are N-H···X hydrogen bonds with N···Cl = 3.114(3) Å and N···Br = 3.270(3) Å. The distances are considerably shorter than the sums of the van der Waals radii, 3.30 and 3.45 Å,[16] respectively, and the two bonds are of corresponding strength. The interactions represent relatively strong hydrogen bonds[17] even though a N···Cl distance of 2.694 Å is observed for N-H···Cl contacts[18] and a N···Br distance of 2.981 Å is observed for N-H···Br contacts.[19] The X···S contacts and the hydrogen bonds are perpendicular to the planes through the selenium and halogen atoms. It is likely that the short X···S contacts in **1** and **2** will reduce the *trans* influence of the halogen atoms, but unknown to what extent since there is no known structure without such contacts. The hydrogen bonds in **3** and **4**, however, seem to have a remarkable effect on the bonding systems. The bridging Se-X bonds are increased by an average of 0.087 Å and the terminal Se-S bonds are decreased by an average of 0.023 Å compared to the isotypic pair **1** and **2**. It is also worth noticing that the increasing asymmetry leads to increase of the S-Se-S bond angles.

Comparison of the compounds within each pair of isotypic structures shows that the bridging bonds are 0.076–0.094 Å longer in the bromine compounds than in the chlorine compounds. The differences are appreciably less than the difference in covalent radii for Br and Cl, 0.15 Å,[16] and this in addition to the fact that the terminal bonds in the bromine compounds are slightly longer than in the chlorine compounds indicates a *trans*-influence order Br>Cl.

Since the bond lengths of **3** and **4** are much more influenced by interionic contacts than **1** and **2** we restrict our comparison with related compounds to the latter. In compounds no. 4 – 7, 11 and 12 of Table III, the terminal thiocyanate groups are replaced by halide ions. In these compounds the bridging Se-X bonds are reduced by an average of 0.177 Å for both halides. This shows that thiocyanate as terminal group has stronger *trans* influence towards chloride and bromide than the halides themselves. This is also seen from the dimensions of compound no. 10 of Table III, where the two 3*c*-4*e* systems are NCS_t-Se-Br_{br} and Br_t-Se-Br_{br}.

In compound no. 1 of Table III all ligands are thiocyanate ions. Comparison of the bond lengths of this compound with those of compounds **1** and **2** shows no significant difference in *trans* influence between thiocyanate and halide as bridging ligands.

If the S_N2 reaction between SeX_2 and SCN^-, which was the basis for the preparation of the present compounds, goes to the end, the final product is $Se(SCN)_2$. The crystal structure of this compound[13] shows great resemblance with the $Se(SCN)_2$ parts of the present structures. In the $Se(SCN)_2$ molecule the S-Se-S angle is a little wider and the Se-S bond lengths are a little shorter. The selenium atom has a short contact to nitrogen of an adjacent molecule. The Se···N distance is 3.000 Å and the S-Se···N sequence is nearly linear. The compound $Se(SCN)_2$ might therefor be looked upon as a neutral complex.

The dimensions of the cations of the present structures do not deviate from the usual values.

TABLE I Crystal data for complexes **1–4**

Complex	*1*	*2*	*3*	*4*
Formula	$C_{22}H_{28}Cl_2N_6S_4Se_2$	$C_{22}H_{28}Br_2N_6S_4Se_2$	$C_{10}H_{20}Cl_2N_6S_4Se_2$	$C_{10}H_{20}Br_2N_6S_4Se_2$
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group (no.)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$Pbca$ (No. 61)	$Pbca$ (No. 61)
a/Å	14.452(2)	14.405(1)	8.927(1)	8.952(1)
b/Å	8.880(2)	8.934(1)	11.498(2)	11.757(1)
c/Å	11.837(1)	12.120(2)	21.929(1)	22 020(2)
β/°	104.78(1)	105.75(1)		
U/Å^3	1468.8(4)	1501.2(3)	2250.8(4)	2317.7(4)
Z	2	2	4	4
μ/mm^{-1}	3.01	5.43	3.90	7.01
T/K	97(2)	111(2)	112(2)	106(2)
Independent reflections	4274	3036	3247	3367
No. with $I > 2\sigma(I)$	3095	2063	2122	2214
$R1$, $wR2$ $[I > 2\sigma(I)]$	0.0397, 0.0970	0.0411, 0.0950	0.0317, 0.0666	0.0315, 0.0713
$R1$, $wR2$ (all data)	0.0808, 0.1109	0.0932, 0.1104	0.0891, 0.0810	0.0812, 0.0831

X-RAY STRUCTURE ANALYSES

The determination of unit cell dimensions and data collections were carried out on an Enraf-Nonius CAD4 diffractometer. Data reductions were undertaken by XCAD4,[9] the structures solved by SHELXS97[10] and refined by SHELXL97.[11] The crystal data, condition for data collection, and refinements are summarised in Table I. The hydrogen atoms were located from the difference maps and refined with isotropic displacement parameters equal to 1.3U(eq) for the atom to which they are attached. All non-hydrogen atoms were refined anisotropically.

TABLE II Bond lengths [Å], bond angles and torsion angles [°] for complexes **1–4**

Compound	*[Se$_2$Cl$_2$(SCN)$_4$]$^{2-}$*		*[Se$_2$Br$_2$(SCN)$_4$]$^{2-}$*	
	1	***3***	***2***	***4***
Se-S(1)	2.2618(9)	2.2535(9)	2.2742(16)	2.2573(10)
Se-S(2)	2.2838(11)	2.2523(9)	2.2952(17)	2.2593(9)
Se-Cl/Br	2.9552(8)	3.0407(9)	3.0440(10)	3.1168(6)
Se-Cl(a)/Br(a)	2.8853(11)	2.9763(9)	2.9709(8)	3.0702(5)
Se···Se(a)	4.2649(8)	4.3116(7)	4.4049(12)	4.4955(7)
S(1)-C(1)	1.691(4)	1.690(4)	1.702(7)	1.689(4)
S(2)-C(2)	1.688(4)	1.688(4)	1.688(7)	1.689(4)
C(1)-N(1)	1.155(5)	1.150(4)	1.134(8)	1.148(5)
C(2)-N(2)	1.157(5)	1.156(5)	1.157(8)	1.154(5)
Cl/Br(b)···S(1)	3.3747(12)		3.4165(16)	
N(3)-H(3)		0.86(4)		0.96(4)
Cl/Br···H(3a)		2.25(4)		2.31(4)
Cl/Br···N(3a)		3.114(3)		3.270(3)
S(1)-Se-S(2)	94.92(3)	95.79(3)	95.14(6)	96.23(4)
S(1)-Se-Cl/Br	174.51(3)	175.79(3)	174.89(5)	176.02(3)
S(1)-Se-Cl(a)/Br(a)	89.71(3)	88.77(3)	89.71(4)	89.73(3)
S(2)-Se-Cl/Br	89.29(3)	87.28(3)	89.34(5)	87.39(3)
S(2)-Se-Cl(a)/Br(a)	175.06(3)	172.81(3)	175.08(5)	172.68(3)
Cl-Se-Cl(a)/Br(a)	86.20(2)	88.46(2)	85.84(2)	86.796(12)
C(1)-S(1)-Se	99.07(12)	98.62(12)	98.7(2)	98.66(13)
C(2)-S(2)-Se	98.48(14)	100.36(13)	97.9(2)	99.80(14)
Se-Cl/Br-Se(a)	93.80(2)	91.54(2)	94.16(2)	93.204(12)
N(1)-C(1)-S(1)	176.9(3)	178.2(3)	176.3(6)	179.2(4)
N(2)-C(2)-S(2)	178.3(4)	177.5(4)	177.1(6)	177.0(4)
Cl/Br···H(3a)-N(3a)		174.9		174.9
S(2)-Se-S(1)-C(1)[a]	−91.21(13)	−86.63(12)	−93.29(21)	−87.13(14)
S(1)-Se-S(2)-C(2)[a]	86.16(12)	92.75(12)	87.82(21)	94.78(14)

Symmetry transformation: (a) 1-*x*, -*y*, -*z* for **1** and **2**; -*x*, 1-*y*, 1-*z* for **3** and **4**; (b) *x*, ½ – *y*, *z* – ½..

a. Torsion angle.

TABLE III Bond lengths [Å] in $Se_2X_6^{2-}$ ions (X = SCN, Cl or Br)

No.	*Compound*	*Terminal bonds*	*Bridging bonds*	*X_t-Se-X_t angle*	*Ref.*
1	$K_2[Se_2(\mu\text{-}SCN)_2(SCN)_4]\cdot\frac{1}{2}H_2O$	2.282(3)	2.953(3)	98.5(1)	1
		2.252(2)	3.112(3)		
		2.318(3)	2.906(3)	95.5(1)	
		2.290(2)	2.907(3)		
2	$[C_6H_5(CH_3)_3N]_2[Se_2(\mu\text{-}Cl)_2(SCN)_4]$ (**1**)	2.262(1)	2.955(1)	94.92(3)	This work
		2.284(1)	2.885(1)		
3	$[(CH_3)_3NH]_2[Se_2(\mu\text{-}Cl)_2(SCN)_4]$ (**3**)	2.254(1)	3.041(1)	95.79(3)	This work
		2.252(1)	2.976(1)		
4	$[Se_4N_3]_2[Se_2(\mu\text{-}Cl)_2Cl_4]$	2.231(4)	2.766(6)	95.5(2)	3
		2.219(4)	2.827(6)		
		2.239(4)	2.815(5)	95.7(2)	
		2.270(4)	2.688(5)		
5	$[(C_6H_5)_4P]_2[Se_2(\mu\text{-}Cl)_2Cl_4]$	2.254(1)	2.739(1)	94.30(3)	4
		2.291(1)	2.620(1)		
6	$[(CH_3)_3SiN(H)P(CH_3)_3]_2[Se_2(\mu\text{-}Cl)_2Cl_4]$	2.268(3)	2.717(3)	95.9(2)	5
		2.268(4)	2.752(4)		

No.	*Compound*	*Terminal bonds*	*Bridging bonds*	*X_t-Se-X_t angle*	*Ref.*
7	$[(C_6H_5)PSH]_2[Se_2(\mu\text{-}Cl)_2Cl_4]$	2.288(2)	2.631(2)	93.7(1)	6
		2.238(2)	2.833(2)		
8	$[C_6H_5(CH_3)_3N]_2[Se_2(\mu\text{-}Br)_2(SCN)_4]$ (2)	2.274(2)	3.044(1)	95.14(6)	This work
		2.295(2)	2.971(1)		
9	$[(CH_3)_3NH]_2[Se_2(\mu\text{-}Br)_2(SCN)_4]$ (4)	2.257(1)	3.117(1)	96.23(4)	This work
		2.259(1)	3.070(1)		
10	$[(C_2H_5)_4N]_2[Se_2(\mu\text{-}Br)_2Br_2(SCN)_2]$	2.260(2)	3.063(1)	93.22(5)	8
		2.493(1)	2.687(1)		
11	$[(C_6H_5)_4P]_2[Se_2(\mu\text{-}Br)_2Br_4]$	2.399(1)	2.887(1)	95.24(2)	2
		2.485(1)	2.710(1)		
12	$[C_6H_5(CH_3)_3N]_2[Se_2(\mu\text{-}Br)_2Br_4]$	2.425(2)	2.865(2)	95.03(6)	7
		2.439(2)	2.792(2)		
		2.404(2)	2.899(2)	95.19(6)	
		2.421(2)	2.834(2)		

Terminal bonds and bridging bonds of a 3*c*-4*e* system are listed in the same line.

PREPARATIONS

$[C_6H_5(CH_3)_3N]_2[Se_2(\mu\text{-}Cl)_2(SCN)_4]$ 1

To a solution of Cl_2 (2.5 mmol, 0.177 g) in acetonitrile (8.0 g) was added Se (2.5 mmol, 0.197 g) and the mixture was stirred. To the eventually clear solution was added $[C_6H_5(CH_3)_3N]SCN$ (5.0 mmol, 0.972 g) whereby some small light yellow crystals separated. The crystals were filtered off and the orange-red solution was left in a freezer. After about 1 h the solution was decanted from a precipitate of colourless crystals and some elementary selenium, and again placed in the freezer. Eventually nice yellow crystals separated. The crystals were washed with dichloromethane and dried. By exposure to air the crystals become orange by decomposition, but they are stable in an atmosphere of argon.

$[C_6H_5(CH_3)_3N]_2[Se_2(\mu\text{-}Br)_2(SCN)_4]$ 2

To a stirred suspension of Se (5.0 mmol, 0.395 g) in nitromethane (3.0 g) was added Br_2(5.0 mmol, 0.799 g) dissolved in nitromethane (2.0 g). The resulting dark brown solution was first placed in a freezer and then in an ice/salt mixture of −15°C. To the stirred solution was added $[C_6H_5(CH_3)_3N]SCN$ (10.0 mmol, 1.944 g) whereby the clear solution became orange-red and small ochre-yellow crystals separated. The crystals were washed with ethyl ether and dried in air. The product was recrystallised from nitromethane whereby nice ochre-yellow crystals precipitated.

$[(CH3)_3NH]_2[Se_2(\mu\text{-}Cl)2(SCN)_4]$ 3

To a solution of Cl_2 (2.5 mmol, 0.177 g) in dichloromethane (13.5 g) was added Se (2.5 mmol 0.197 g) and the mixture was stirred. When all the selenium was dissolved, $[(CH_3)_3NH]SCN$ (5.0 mmol, 0.591 g) was added with stirring. From the clear orange-red solution small ochre-yellow crystals separated. The crystals were filtered off, washed with dichloromethane and dried in air. By recrystallisation from nitromethane some colourless crystals remained undissolved and from the decanted solution nice ochre-yellow crystals precipitated.

$[(CH_3)_3NH]_2[Se_2(\mu\text{-}Br)_2(SCN)_4]$ 4

To a stirred suspension of Se (5.0 mmol, 0.395 g) in acetonitrile (3.0 g) was added Br_2 (5.0 mmol, 0.799 g) dissolved in acetonitrile (2.0 g). The resulting solution soon became dark brown. It was placed in a freezer for about 1 h, and then in an ice/salt mixture of −15°C. To the stirred solution was added $[(CH_3)_3NH]SCN$ (10.0 mmol, 1.182 g). From the resulting clear orange-red solution small ochre-yellow crystals separated. The crystal were washed with dichloromethane and dried in air. By recrystallisation from nitromethane some colourless crystals remained undissolved and from the decanted solution nice ochre-yellow crystals precipitated.

$[C_6H_5(CH_3)_3N]_2[SeBr_4]$ 5

To a stirred suspension of Se (5.0 mmol, 0.395 g) in acetonitrile (3.0 g) was added Br_2 (3.3 mmol, 0.527 g) dissolved in acetonitrile (2.0 g), followed by $[(CH_3)_3NH]SCN$ (10.0 mmol, 1.182 g). The crystals formed at room temperature were very small and seemed to be a mixture of different compounds. The filtrate was placed in a freezer and eventually some crystals were isolated and characterised by X-ray analyses as $[C_6H_5(CH_3)_3N]_2[SeBr_4]$.

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