Crystal structure of tris(o-phenylenethiourea)selenium(II) bromide pentahydrate, $C_{21}H_{18}N_6S_3Br_2Se \cdot 5H_2O$

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The synthesis and crystal structure of the title complex are reported. Crystals are triclinic, space group $P\bar{1}$ with $a = 10.359(2)$, $b = 10.742(2)$, and $c = 13.604(2)$ A, $\alpha = 87.25(1)$, $\beta = 88.89(1)$, $\gamma = 83.63(2)°$, and $Z = 2$. The structure was solved by the heavy atom method and refined by least squares to final R and R_w of 0.055 and 0.06 for 1707 unique reflections. The structure is comprised of planar $[Se_2(o\text{-phenylenethiourea})_6]^{4+}$ ions and bromide counterions with the water molecules providing extensive lattice stabilization through hydrogen bonding. The dinuclear complex arises by the fusion of two SeS_4 trapezoids with each Se bonded strongly to two terminal sulfur atoms Se—S(1) = 2.306(4), Se—S(3) = 2.286(5) Å and weakly to two other bridging sulfur atoms Se—S(2) = 2.840(5) and Se—S(2)' = 2.852(5) Å.

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On rapporte la synthèse et la structure cristalline du complexe mentionné dans le titre. Les cristaux sont tricliniques et cristallisent dans le groupe d'espace $P\bar{1}$ avec $a = 10,359(2)$, $b = 10,742(2)$, et $c = 13,604(2)$ Å, $\alpha = 87,25(1)$, $\beta = 88,89(1)$, $\gamma = 83,63(2)°$, et $Z = 2$. On a résolu la structure par la méthode des atomes lourds et on l'a affinée par la méthode des moindres carrés jusqu'a des valeurs finales de R et R_w de 0,055 et 0,06 pour 1707 réflexions uniques. La structure comporte des ions plans de $[Se_2(o\text{-phénylènethiourée})_6]^{4+}$ et des contre-ions bromures avec des molécules d'eau qui fournissent une stabilisation importante de la maille par le biais de liaisons hydrogènes. Le complexe binucléaire provient de la fusion de deux SeS_4 sous forme de trapézoïdes dans lesquels chacun des Se est fortement lié aux deux atomes de soufre terminaux (Se—S(1) = 2,306(4) et Se—S(3) = 2,286(5) Å) et faiblement lié à deux autres atomes de soufre qui agissent comme ponts (Se—S(2) = 2,840(5) et Se—S(2)' = 2,852(5) Å).

[Traduit par le journal]

Introduction

The interaction of selenium(IV) species with sulfur ligands has gained immense importance due to the formation of the Se(II)–sulfur ligated complexes which have been shown to be intermediates in the biochemical role of selenium (1, 2). Generally the interaction of selenium(IV) with sulfur containing ligands leads either to (*a*) reductive complexation, that is, reduction of selenium(IV) to selenium(II) and formation and stabilization of selenium(II) complexes with sulfur ligands (eg., thiosulphate (3), xanthates (4), dithiocarbamates (5), thiobenzoic acid (6), mercaptocarboxylic acids (7)) or to (*b*) reduction to elemental selenium (eg., hydrogen sulphide, thiourea). Very recently, with the use of concentrated hydrochloric acid medium, the highly unstable complex *cis*-dichlorobis(thiourea)-selenium(II) was isolated (8), and its structure determined. We have found (9) that, unlike thiourea, interaction of *o*-phenylene-thiourea (ptu) with Se(IV) species leads to ready formation of Se(II) complexes, which are indefinitely stable at room temperature. In this paper we report the synthesis and structure of tris(*o*-phenylenethiourea)selenium(II) bromide pentahydrate. The structure consists of novel planar Se_2S_6 units (the first of its kind to be reported in Se(II) complexes with unidentate ligands) containing four moderately strong Se—S terminal bonds and four loose bridging Se—S bonds with each Se(II) displaying a trapezoidal sulfur coordination.

Experimental

Preparation of the complex

The reaction used for the preparation of the complex is

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[1]
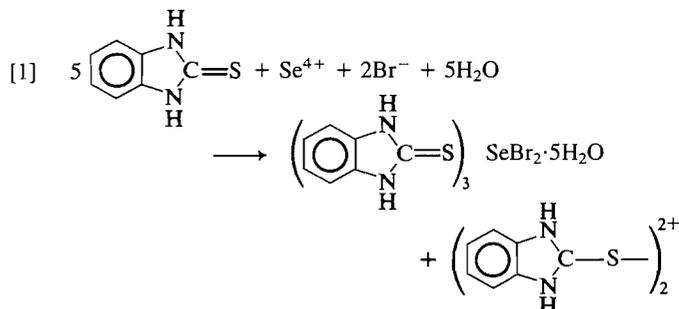
SeO_2 (BDH, 0.5 mmol (0.055 g)) dissolved in 3 mL of methanol and of *o*-phenylenethiourea (Aldrich Co. 99% pure, 3 mmol (0.45 g)) dissolved in 15 mL of methanol were mixed in the presence of 12.5 mL of 2 *N* hydrobromic acid. The yellow solution obtained, gave needle shaped, yellow-orange crystals of the title complex on evaporation at room temperature (30°C). *Anal.* calcd.: Se 10.14, Br 20.54, S 12.32, N 10.78. C 32.24, H 3.59; found: Se 10.09, Br 20.48, S 12.34, N 10.70, C 32.21, H 3.96. To prevent contamination with excess ligand or oxidized product, the crystals formed were washed with ether. The crystals were extremely stable when preserved in paraffin. In dry atmosphere, the crystals turned opaque and brittle due to loss of water of crystallization.

It is interesting to report that the disulfide oxidation product in reaction [1] was found to undergo disproportionation rapidly under acidic

conditions to *o*-phenylenethiourea and a
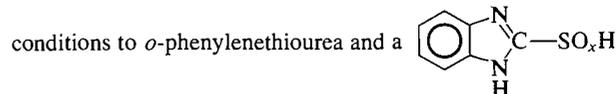
species, determination of whose composition and detailed characterization is in progress.

87.25(1), β = 88.89(1), γ = 83.63(2)°, V = 1502.6 Å^3. Space group $P\bar{1}$, Z = 2, $F(000)$ = 919.99, D_x = 1.72 Mg m^{-3}, $\mu(MoK_\alpha)$ = 4.11 mm^{-1}. Preliminary cell constants were obtained from Weissenberg photographs and a crystal of size 0.42 × 0.25 × 0.22 mm was mounted on a Enraf–Nonius CAD 4 diffractometer. Graphite monochromated MoK$_\alpha$(λ = 0.71069 Å) radiation was used. Lattice parameters were determined by least-squares refinement of θ values of 25 high angle reflections. The intensity data were collected by ω–2θ scan technique with scan interval $\Delta\omega$ = (0.80 + 0.35 tan θ)°, extended by 25% on both sides for background measurements. Two check reflections (42$\bar{6}$ and 06$\bar{1}$) recorded at the end of every hour of data collection time, showed no significant variation in intensity. A total of 5763 reflections were collected in the range of 2 < θ < 25° (h, 0–12; k, −12–12; 1, −16–16). The 1707 reflections with I > 3$\sigma(I)$ formed a unique set. R_{int} equalled 0.01 after merging 123 reflections. No correction was made for absorption.

The SHELX-76 program (10) was used for all the computations done in solving the structure. Se and Br atoms were located from a Patterson map and the rest of the structure from Fourier maps. The function minimized in full matrix least-squares refinement was $\Sigma\omega(\Delta F)^2$. All but seven of the hydrogen atoms appeared in the final difference Fourier maps and were refined isotropically. Maximum peak height in the final difference Fourier map was 0.73 e Å^{-3}, maximum and average shift/esd in all non-hydrogen atom parameters were 1.615 and 0.022 in the final refinement cycle. Convergence was reached at R = 0.055 and R_w = 0.06 where w (the weighting scheme used) = $1/(\sigma^2(F_o) + 0.0599|F_o|^2)$.

Though the crystal used was of good quality as shown by the photographs and reflection profiles, only 30% of the possible reflections were observed, indicating that the diffractometer alignment should have been better, which would have yielded better quality data. This is also reflected in the large shift/esd in refinement, the data/parameter ratio being only 4.0.

Atomic scattering factors for non-hydrogen atoms, hydrogen atoms, and anomalous scattering factors are taken from refs. 11, 12, and 13, respectively.

The final positions are given in Table 1. Table 2 contains the bonding parameters in the structure. Fig. 1 was drawn using the ORTEP (14) program[3].

Results and discussion

Crystals of Se(ptu)$_3$Br$_2$·5H$_2$O are yellow-orange in colour, this being attributed to typical charge transfer bands. The compound is stable as such or when suspended in 2 N hydrobromic acid, but undergoes an immediate self-redox decomposition to Se and an oxidized product of the ligand when immersed in alkaline solution. The infrared spectrum of the complex does not have distinctive differences from that of the ligand which would enable positive conclusions regarding the coordination behaviour of the ptu ligand in the complex.

Figure 1 shows the ORTEP picture of the molecule. Only half of the centrosymmetrical [Se$_2$(ptu)$_6$]$^{4+}$ unit is featured in full. Additionally, the selenium and three sulfur atoms belonging to the other half are also shown for reasons of clarity. The structure is made up of an [Se$_2$(ptu)$_6$]$^{4+}$ cation, bromide counterions, and five water molecules of crystallization. In each cation, selenium, the soft acid site, is bonded to four phenylenethiourea ligands exclusively through sulfur atoms, the soft base site. The dinuclear complex arises by the fusion of two SeS$_4$ trapezoids with each selenium bonded strongly to two terminal sulfur atoms Se—S(1) = 2.306(4), Se—S(3) = 2.286(5) Å and

TABLE 1. The fractional atomic coordinates (×10^4) and equivalent thermal parameters (×10^3 Å^2) of nonhydrogen atoms

Atoms	X	Y	Z	U_{eq}
Se	314(1)	6884(2)	4733(1)	36(1)
Br(1)	3227(3)	373(3)	7944(2)	116(1)
Br(2)	−2208(2)	4556(2)	2614(2)	83(1)
S(1)	−1142(4)	8672(4)	4721(3)	48(2)
S(2)	1825(4)	4509(4)	4807(3)	44(1)
S(3)	2148(4)	7833(4)	4383(3)	45(1)
C(1)	−1336(17)	8785(13)	5999(12)	44(6)
N(1)	−2517(14)	8856(13)	6434(11)	51(6)
N(2)	−379(14)	8914(12)	6661(10)	42(5)
C(11)	−2288(18)	8990(15)	7439(14)	45(7)
C(12)	−1020(16)	9021(15)	7580(12)	47(6)
C(13)	−437(21)	9136(17)	8507(14)	62(8)
C(14)	−1337(23)	9202(19)	9280(15)	65(9)
C(15)	−2645(24)	9168(20)	9171(15)	72(9)
C(16)	−3244(22)	9082(17)	8250(16)	71(8)
C(2)	1976(17)	4425(16)	3548(12)	41(6)
N(3)	3110(12)	4456(13)	3046(10)	37(5)
N(4)	1018(12)	4244(12)	2918(9)	32(4)
C(21)	2905(18)	4336(15)	2051(14)	46(7)
C(22)	1579(16)	4253(14)	1962(13)	39(6)
C(23)	980(20)	4114(17)	1043(11)	55(7)
C(24)	1849(21)	4107(19)	228(13)	58(8)
C(25)	3156(22)	4277(18)	333(14)	63(8)
C(26)	3707(18)	4363(17)	1247(15)	56(7)
C(3)	2346(16)	7685(15)	3103(11)	42(6)
N(5)	3518(13)	7763(13)	2661(10)	50(6)
N(6)	1466(13)	7525(13)	2458(10)	44(5)
C(31)	3369(18)	7695(16)	1679(14)	44(7)
C(32)	2132(16)	7545(16)	1508(14)	46(6)
C(33)	1598(20)	7443(16)	575(14)	59(7)
C(34)	2460(22)	7492(19)	−207(15)	58(8)
C(35)	3744(26)	7682(18)	−46(16)	81(10)
C(36)	4267(19)	7769(17)	904(15)	93(8)
O(1)	−4969(15)	8784(21)	5646(12)	136(9)
O(2)	2309(16)	8322(14)	6648(12)	102(7)
O(3)	5293(15)	4494(30)	4079(13)	205(15)
O(4)	5777(14)	7665(18)	3714(12)	120(8)
O(5)	−1145(15)	7354(15)	2218(11)	100(7)

weakly to two other bridging sulfur atoms Se—S(2) = 2.840, Se—S(2)' = 2.852 Å. The SeS$_4$ group is planar to within 0.007 Å. The S—Se—S angles deviate substantially from 90°. The dihedral angle between the two SeS$_4$ trapezoids is nearly zero (0.03 (20)°). It is the first time in selenium(II) chemistry that a dimeric structure is reported with monodentate sulphur ligands. A [Te$_2$S$_6$]$^{4+}$ dimer with similar molecular geometry was reported (15) in the compound Te(tu)$_3$(HF$_2$)$_2$ (tu = thiourea).

It is interesting to comment on the coordination types of sulfur ligands reported till now around Se(II). The coordination number is observed to be two (bent) or four (square planar or trapezoidal). In two coordinated Se(II) complexes, the Se—S bond lengths are close to the sum of single covalent radii of selenium and sulfur (2.11 Å) as reported in refs. 3, 6, 7, 8, 16, and 17. This is because the ligands in these cases are mostly negatively charged and unidentate, and there are only two sulfur ligands bonded to selenium. In Se(S$_2$COCH$_3$)$_2$ (4) xanthate provides four sulfur atoms around the central metal atom selenium, two of these sulfurs (bridging ligands) are quite far from selenium so that their interaction with selenium is very weak, enabling the other thiolatosulfurs to bond strongly. Complexes such as Se(S$_2$CNC$_4$H$_8$O$_2$)$_2$ (5) and Se[N(Ph$_2$PS)$_2$]

TABLE 2. Bond lengths (Å) and bond angles (°), esd in parentheses

Atoms	Bond length	Atoms	Bond length
Se—S(1)	2.306(4)	C(21)—C(22)	1.394(25)
Se—S(2)	2.840(4)	C(22)—C(23)	1.428(24)
Se—S(3)	2.286(5)	C(23)—C(24)	1.414(26)
S(1)—C(1)	1.755(17)	C(24)—C(25)	1.397(32)
C(1)—N(1)	1.345(23)	C(25)—C(26)	1.390(29)
C(1)—N(2)	1.375(23)	C(26)—C(21)	1.362(24)
N(1)—C(11)	1.398(25)	C(3)—N(5)	1.354(21)
N(2)—C(12)	1.408(21)	C(3)—N(6)	1.308(21)
C(11)—C(12)	1.354(25)	N(3)—C(21)	1.389(24)
C(12)—C(13)	1.425(26)	N(4)—C(22)	1.414(21)
C(13)—C(14)	1.390(29)	N(5)—C(31)	1.354(24)
C(14)—C(15)	1.371(35)	N(6)—C(32)	1.454(23)
C(15)—C(16)	1.420(31)	C(31)—C(32)	1.335(26)
C(16)—C(11)	1.463(29)	C(32)—C(33)	1.408(27)
S(2)—C(2)	1.723(17)	C(33)—C(34)	1.378(30)
C(2)—N(3)	1.350(21)	C(34)—C(35)	1.391(36)
C(2)—N(4)	1.360(22)	C(35)—C(36)	1.422(31)
S(3)—C(3)	1.762(16)	C(36)—C(31)	1.398(27)

Atoms	Angle	Atoms	Angle
S(2)—Se—S(3)	89.9(2)	C(2)—N(3)—C(21)	110(1)
S(1)—Se—S(2)	172.6(2)	C(2)—N(4)—C(22)	107(1)
S(1)—Se—S(3)	97.6(2)	N(3)—C(21)—C(22)	106(1)
S(1)—Se—S(2')	87.6(2)	N(4)—C(22)—C(21)	108(1)
S(2)—Se—S(2')	85.0(3)	C(21)—C(22)—C(23)	123(1)
S(3)—Se—S(2')	174.8(2)	C(22)—C(23)—C(24)	114(1)
Se—S(1)—C(1)	97.8(7)	C(23)—C(24)—C(25)	122(1)
S(1)—C(1)—N(1)	121(1)	C(24)—C(25)—C(26)	122(1)
S(1)—C(1)—N(2)	127(1)	C(25)—C(26)—C(21)	117(1)
C(1)—N(1)—C(11)	106(1)	Se—S(3)—C(3)	102.9(6)
C(1)—N(2)—C(12)	105(1)	S(3)—C(3)—N(5)	121(1)
N(1)—C(11)—C(12)	109(1)	S(3)—C(3)—N(6)	128(1)
N(2)—C(12)—C(11)	108(1)	N(5)—C(31)—C(32)	109(1)
C(11)—C(12)—C(13)	125(1)	N(6)—C(32)—C(31)	107(1)
C(12)—C(13)—C(14)	113(1)	C(31)—C(32)—C(33)	126(1)
C(13)—C(14)—C(15)	124(2)	C(32)—C(33)—C(34)	115(1)
C(14)—C(15)—C(16)	124(2)	C(33)—C(34)—C(35)	120(1)
C(15)—C(16)—C(11)	113(2)	C(34)—C(35)—C(36)	124(1)
Se—S(2)—C(2)	95(1)	C(35)—C(36)—C(31)	115(1)
S(2)—C(2)—N(3)	124(1)	Se—S(2)'—Se'	95.0(2)
S(2)—C(2)—N(4)	126(1)		

(18) though arising from bidentate ligands, are structurally very close to the present case, which have two weaker and two stronger bonds in its four coordination leading to a planar trapezoidal structure. [Se(ptu)$_4$]Cl$_2$·2HCl (9) is the only complex so far reported in Se(II) chemistry which shows a near square planar coordination. In the present case, in which the same sulfur compound features as the ligand, the smaller number of ligands per Se(II) alters the molecular geometry of SeS$_4$ coordination from square planar to trapezoidal and also provides a dimeric Se$_2$S$_6$ unit. In all the SeS$_4$ species the average Se—S bond length is 2.53 Å, showing that the Se—S interactions in these complexes are weaker than in two-coordinated complexes. This can be attributed to the larger number of sulfur atoms around selenium in the tetra-coordinated complexes.

The ptu ligands are planar to within 0.04 to 0.07 Å. The C—S distances in the ligands are 1.75(2), 1.72(2), and 1.76(2) Å showing partial double bond character. The C(1)—N(1) and

C(1)—N(2); C(2)—N(3) and C(2)—N(4); C(3)—N(5) and C(3)—N(6) pairs show no significant variation in bond lengths, clearly indicating that the ptu ligand in the Se(II) complex occurs exclusively in thione form with the molecular parameters close to those observed in the structure of the free ptu ligand (19), Se(ptu)$_4$·Cl$_2$·2HCl (9), and in tellurium(II) complexes of the ligand (20). The ligand in all these cases is present in the thione form. The other bond parameters in the ligands are normal. The average N—H, C—H, and O—H bond lengths are 0.88(7), 0.91(2), and 0.83(1) Å, respectively.

There are two bromide ions per formula unit. The bromines, water oxygens, and nitrogen atoms of ptu ligand form an extensive hydrogen bonding network. Bromine atoms are well outside the coordination sphere of Se and form hydrogen bonds with six water molecules and one nitrogen atom, with Br...O and Br...N distances in the range of 3.08(2)–3.33(2) and 3.35(1) Å, respectively. The angles Br...H—O are in between 157 and 175° and the Br...H—N angle is 128°. Also oxygen
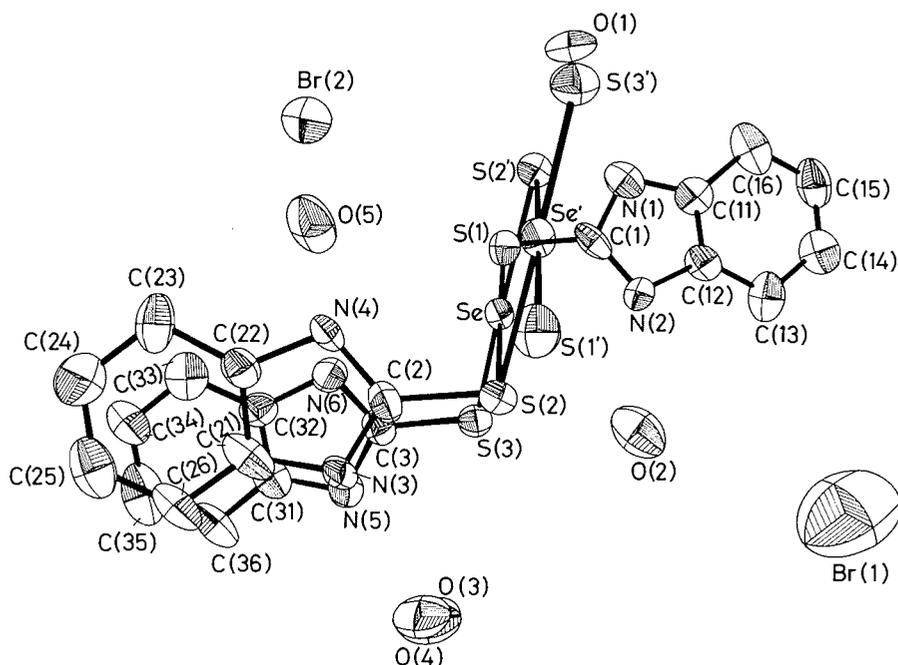
FIG. 1. Perspective view of the molecule showing atomic numbering, with 50% probability thermal ellipsoids.

atoms of water molecules form five hydrogen bonds with nitrogen atoms, as evidenced by the N...O distances of the order of 2.69(2) Å. N—H...O angles range between 163 and 176°. In addition, oxygen atoms among themselves form two hydrogen bonds with O...O distances 2.99(2) and 2.81(3) Å.

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