Crystal and Molecular Structures of *trans*-Dibromobis(1,4-oxathian)-platinum(II) and *trans*-Dibromobis(1,4-oxaselenan)platinum(II)

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The structures of the title compounds have been determined by heavy-atom *X*-ray methods. Both complexes are monomeric, square-planar platinum(II) compounds. They differ in configuration, the oxathian complex (I) has the Pt–S bond (2.281 Å) equatorial to the ring whereas in the oxaselenan complex (II) the Pt–Se bond (2.430 Å) adopts the axial position. Crystal data : (I), space group $P2_1/n$, a = 4.515(5), b = 19.717(10), c = 7.609(5) Å, β = 97.2(2)°, Z = 2 ; (II), space group $P2_1/c$, a = 6.36(1), b = 10.47(2), c = 10.80(2) Å, β = 102.1(1)°, Z = 2. The structures were refined by least-squares methods to R 0.065 [(I), 872 reflections (photographic)] and 0.069 [(II), 596 reflections (diffractometer)].

1,4-OXATHIAN (tx) and 1,4-oxaselenan (sx) are much less catholic than 1,4-dioxan in the range of metal ions with which they form complexes. Of the few complexes which have been reported the only crystal structure studied is that of tetrahedral [$HgCl_2(tx)_2$].[1] The structures of *trans*-[$PtBr_2(tx)_2$] (I) and *trans*-[$PtBr_2(sx)_2$] (II) have now been determined. These complexes are of current interest because conformational n.m.r. studies in solution[2] showed a marked difference in the thermodynamic parameters for site inversion between (I) and (II). These complexes are also of interest in conjunction with studies of potentially bridging six-membered ring ligands,[3,4] and work on unidentate ligands about platinum(II) halides.[5,6]

EXPERIMENTAL

The crystals of both compounds were available from previous work.[2] Both compounds are air- and radiation-stable.

Crystal Data for (I).—$C_8H_{16}Br_2O_2PtS_2$, Monoclinic, M = 563.24, a = 4.515(5), b = 19.717(10), c = 7.609(5) Å, β = 97.2(2)°, U = 672.2 Å^3, Z = 2, D_c = 1.68, Cu-K_α radiation, λ = 1.5418 Å; μ(Cu-K_α) = 278 cm^{-1}. Space group $P2_1/n$ from systematic absences: $0k0$ for $k = 2n + 1$, and $h0l$ for $h + l = 2n + 1$.

Intensity data were collected from equi-inclination Weissenberg photographs with the help of the S.R.C. Microdensitometer Service. Unit-cell parameters were refined as part of the intensity measurement and correlation procedure. Data were collected for crystals mounted on the a (0—$2kl$) and c ($hk0$—4) axes. The crystals showed well-developed (100), (010), (011), and (0$\bar{1}$1) faces, distances between parallel faces being 0.10, 0.08, 0.26, and 0.26 mm. Data reduction and much of the subsequent computing was carried out on the Dundee University I.C.L. 4130 computer using the program system of Sheldrick.[7]

Determination of Structure of (I).—872 reflections were recorded as observed above background. The structure was solved by conventional heavy-atom methods. An initial structure-factor calculation phased by the platinum, bromine, and sulphur atom co-ordinates gave R 0.27. The remaining non-hydrogen atoms were then located on a Fourier map and the structure refined to R 0.16 with isotropic thermal parameters for all atoms. After data were corrected for absorption and anomalous dispersion, full-matrix least-squares refinement continued to convergence at R 0.065, with anisotropic thermal parameters for the heavy atoms. Hydrogen atoms were not located. The final weighting scheme used was $w = 1/(\sigma_F^2 + 0.0050F^2)$.

Crystal Data for (II).—$C_8H_{16}Br_2O_2PtSe_2$, Monoclinic, M = 657.02, a = 6.36(1), b = 10.47(2), c = 10.80(2) Å, β = 102.1(1)°, U = 703.11 Å^3, Z = 2, D_c = 3.03. Mo-K_α radiation, λ = 0.710 69 Å; μ(Mo-K_α) = 202 cm^{-1}. Space group $P2_1/c$ from systematic absences: $h0l$ for $l = 2n + 1$, and $0k0$ for $k = 2n + 1$.

After initial examination by rotation and Weissenberg photographs unit-cell dimensions were refined on a Hilger and Watts linear diffractometer, which was used to collect intensity data for b ($h0$—$9l$) and c ($hk0$—6) axis crystals. The crystals showed developed (100), (010), and (001) faces, with dimensions 0.15 ± 0.03 mm in each direction.

Determination of Structure of (II).—There were 596 reflections with $I > 2\sigma$. After application of Lorentz and polarisation corrections common scale factors were obtained for the two crystals. The structure was solved by heavy-atom methods. A structure-factor calculation phased by the platinum, bromine, and selenium atoms gave R 0.32.

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[7] G. M. Sheldrick, personal communication.

Remaining non-hydrogen atoms were located on a Fourier map and the structure refined by use of a local block-diagonal least-squares program to R 0.17, with isotropic thermal parameters. Allowance for anomalous dispersion and the introduction of anisotropic thermal parameters for the heavy atoms in full-matrix least-squares refinement gave convergence at R 0.069. The final weighting scheme used was: $w = 16.23/(\sigma_F^2 + 0.000\,30F^2)$.

In both structures the atomic scattering factors used were taken from ref. 8. Structure factors are listed in Supplementary Publication No. SUP 21903 (11 pp., 1 microfiche).*

DISCUSSION

Atomic co-ordinates and thermal parameters for (I) and (II) are given in Tables 1 and 2. (I) and (II) are typical square-planar platinum(II) complexes. In each case the space group and cell volume specified that the crystals contained the *trans*-isomer although the present samples of (I) and $[PtCl_2(tx)_2]$ gave i.r. spectra identical with those reported by Walton,[9] who interpreted the spectra as those of the *cis*-isomers.

TABLE 1

Atomic co-ordinates (× 10^4) and isotropic thermal parameters (× 10^3) for (I), dibromobis(1,4-oxathian)-platinum(II), with estimated standard deviations in parentheses

	x/a	y/b	z/c	U/Å^2
Pt	0	0	0	*
Br	3 061(4)	715(1)	2 081(2)	*
S	2 393(9)	−870(1)	1 558(6)	*
C(1)	1 063(37)	−1 698(6)	794(23)	39(3)
C(2)	2 129(42)	−2 213(7)	2 162(23)	48(4)
C(3)	761(37)	−883(6)	3 635(25)	40(3)
C(4)	1 869(40)	−1 524(7)	4 718(22)	42(3)
O	800(29)	−2 128(5)	3 809(16)	48(3)

* Anisotropic thermal parameters (Å^2 × 10^4) in the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt	274(6)	308(5)	284(7)	−22(2)	13(5)	−16(2)
Br	444(10)	421(8)	391(11)	−55(8)	−58(8)	−56(6)
S	284(17)	334(13)	356(20)	−16(12)	3(17)	−26(10)

The bond lengths and bond angles in (I) and (II) (Table 3) are all close to the accepted values. The presence of the heavy platinum and bromine atoms leads to the light-atom positions being ill-defined but the dimensions of the heterocycles are in good agreement with those found previously.[1,10,11]

The bond lengths about platinum in (I) can be compared with those in the sulphur-bridged complex $[Pt_2Br_4(SEt_2)_2]$,[12] where Pt–Br are 2.38 and 2.40 Å and Pt–S 2.21 and 2.25 Å against Pt–Br 2.420 and Pt–S 2.281 Å in (I).

Neither (I) nor (II) contain Pt · · · Pt interactions. In (I) the $PtBr_2S_2$ planes are parallel but the Pt · · · Pt distance is 4.515 Å and S–Pt · · · Pt 45°. In (II) the packing precludes Pt · · · Pt contact.

Figures 1 and 2 and Table 4 indicate that (I) and (II) differ in conformation. In (I) the sulphur-containing ligand bonds equatorially to platinum whereas the selenium-containing ligand in (II) adopts the axial configuration. Since (II) differs from (I) only in the replacement of sulphur by selenium, intermolecular packing cannot explain this difference. The packing in (II) is

TABLE 2

Atomic parameters (× 10^4) and isotropic thermal parameters (× 10^3) for (II), dibromobis(1,4-oxaselenan)-platinum(II), with estimated deviations in parentheses

	x/a	y/b	z/c	U/Å^2
Pt	0	0	0	*
Br	2 886(5)	−1 566(3)	134(3)	*
Se	2 270(5)	1 504(3)	1 389(3)	*
C(1)	3 629(68)	−385(35)	3 433(39)	49(8)
C(2)	4 572(39)	603(24)	2 551(24)	31(5)
C(3)	909(59)	1 871(31)	2 706(33)	47(7)
C(4)	475(57)	674(35)	3 505(35)	50(8)
O	2 467(33)	261(18)	4 181(20)	38(4)

* Anisotropic thermal parameters (Å^2 × 10^4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt	246(6)	271(8)	236(7)	15(7)	93(6)	16(7)
Br	349(15)	415(16)	434(16)	−2(14)	98(14)	86(14)
Se	381(16)	342(16)	379(16)	−3(13)	77(14)	−64(14)

TABLE 3

Bond lengths (Å) and bond angles in (I) and (II), with estimated standard deviations in parentheses

(*a*) Distances *	(I)	(II)
Pt–Br	2.420(1)	2.442(3)
Pt–D	2.281(3)	2.430(2)
C(2)–D	1.81(1)	1.96(2)
C(3)–D	1.82(2)	1.86(4)
C(1)–C(2)	1.49(2)	1.61(6)
C(1)–O	1.47(2)	1.38(6)
C(3)–C(4)	1.56(2)	1.58(5)
C(4)–O	1.43(2)	1.39(3)
(*b*) Angles		
D–Pt–Br	84.4(1)	93.3(1)
C(2)–D–Pt	113.2(5)	110.5(7)
C(3)–D–Pt	104.0(4)	107.2(10)
C(2)–D–C(3)	96.4(7)	90.8(13)
C(2)–C(1)–O	112.8(13)	110.2(28)
C(1)–O–C(4)	111.1(13)	112.7(26)
O–C(4)–C(3)	110.7(11)	106.8(29)
C(4)–C(3)–D	109.5(11)	114.7(27)

* D = S in (I), Se in (II).

TABLE 4

Torsion angles (°) * involving the heterocyclic ligand in (I) and (II)

Atom	(I)	(I)
D–C(3)–C(4)–O	69.6	66.4
D–C(2)–C(1)–O	62.2	64.8
Pt–D–C(3)–C(4)	58.8	164.8
Pt–D–C(2)–C(1)	60.6	171.8
Idealised A–X–C(3)–C(4) †	68.6, 164.9	62.0, 173.6

* The torsion angle A–B–C–D is given as the angle between the vector A · · · B and the vector D · · · C seen down the vector B · · · C. † These angles were estimated by calculating the positions of two dummy atoms A in a plane perpendicular to the C(2)–C(3)–D plane. The angles *ca.* 65 and 170° represent axial and equatorial directions respectively.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

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significantly less efficient, resulting in an increase in cell volume greater by 3% than the change required by the substitution.

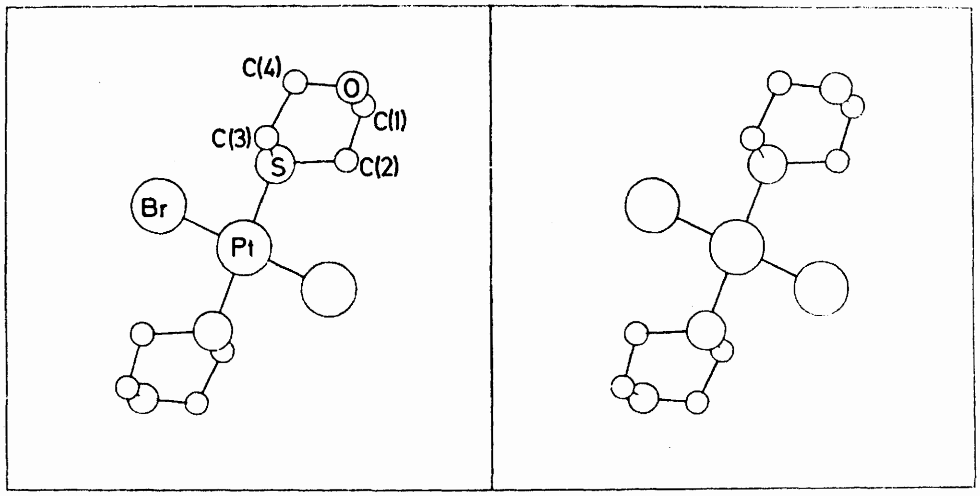

FIGURE 1 [$PtBr_2(C_4H_8OS)_2$] projected on the Pt,Br,S plane

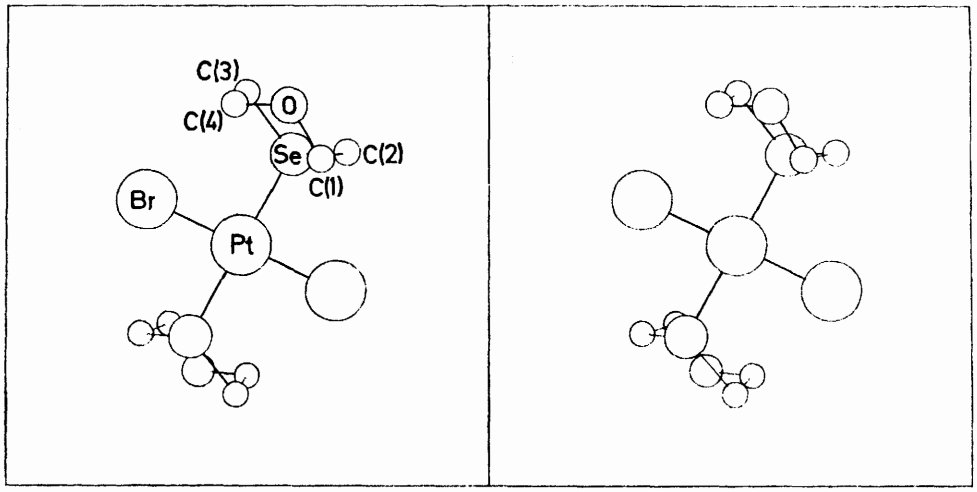

FIGURE 2 [$PtBr_2(C_4H_8OSe)_2$] projected on the Pt,Br,Se plane

Axial selenium and equatorial sulphur bonding are known in other crystal structures. The halogen complexes of oxaselenan[10,11] and diselenan[13] contain axial bonds whereas the iodine complexes of dithian[14] and dioxan[15] are equatorial. In solution, n.m.r. studies of the configurations adopted by light-atom substituents of six-membered heterocycles have shown[16,17] that the axial isomer predominates at selenium, the equatorial isomer at oxygen, and both occur at sulphur in similar compounds. Lambert *et al.*[17] have considered the interaction between an axial substituent and the β-methylene groups of the ring. Replacement of sulphur by selenium increases these non-bonding distances which then lie in the attractive region of a Morse-like potential function describing this interaction. In (II) C(1) $\cdots$ Pt 3.96 and C(4) $\cdots$ Pt 3.80 Å, are very similar to the corresponding carbon–iodine distances in I_2·sx,[10] 3.96 and 3.86 Å. A calculation on (I), altering the conformation to axial, but preserving the Pt–S bond length, suggests that Pt $\cdots$ C(1) and Pt $\cdots$ C(4) distances in an axial thioxan complex would be only *ca.* 3.2 Å.

It seems likely that this conformational difference between (I) and (II) found in the crystal is preserved in solution and that this explains the difference in the thermodynamic parameters for site inversion reported previously.[2]

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