pyrazole rings. The two planes in the dimer are parallel to each other, but the second plane rotates about the Pd(1)—Pd(2) vector relative to the first by 39·3° leading to a staggered conformation. The rotation appears necessary for hydrogen bonding, in addition to the reduction of steric hindrance among the intermolecular ligands. As a consequence of the hydrogen bonds, all the N—H groups lie between the two planes, although such an arrangement would somewhat raise the repulsion between intermolecular pyrazole ligands. All four Pd—Cl bonds are equivalent within experimental error, as are the Pd—N bonds. These bond lengths are comparable with the reported values for Pd—Cl of 2·297 (1) Å and for Pd—N of 2·030 (3) Å in [Pd{$(CH_3)_2C(C_3H_3N_2)_2$}Cl_2] (Minghetti, Cinellu, Bandini, Banditelli, Demartin & Manassero, 1986).

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Structure and Pseudosymmetry of Tetrabromobis(dimethyl sulfoxide)tin(IV)

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Abstract. [$SnBr_4(C_2H_6OS)_2$], $M_r = 594{\cdot}6$, monoclinic, $P2_1/n$, $a = 7{\cdot}7728$ (6), $b = 14{\cdot}676$ (2), $c = 13{\cdot}632$ (2) Å, $\beta = 91{\cdot}11$ (1)°, $V = 1554{\cdot}8$ (5) Å^3, $Z = 4$, $D_x = 2{\cdot}54$, $D_m = 2{\cdot}55$ (2) g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 118{\cdot}42$ cm^{-1}, $F(000) = 1096$, room temperature, $R = 0{\cdot}076$ for 1260 unique reflections with $F > 6\sigma F$. The structure is isomorphous with [$SnCl_4(C_2H_6OS)_2$] and consists of monomeric molecules with *cis*-octahedral coordination around Sn. The dimethyl sulfoxide ligands are bonded through O with Sn—O bond distances [2·153 (15) and 2·205 (15) Å] longer and S—O bond distances [1·507 (13) and 1·487 (14) Å] shorter than in [$SnCl_4(C_2H_6OS)_2$], indicating that the Sn—dmso bond is weaker in the present compound. The Sn—Br bond lengths vary between 2·531 (3) and 2·549 (3) Å. The pseudosymmetry $C2/c$ is related to the existence of two concurrent packing models.

Introduction. The Sn—Cl distance in octahedral tin(IV) chloride complexes is related to the quadrupole splitting in the Mössbauer spectra (Tudela, Khan & Zuckerman, 1989). In the case of tin(IV) bromide complexes, few experimental data are available and more crystallographic and Mössbauer measurements are necessary before a similar relationship can be searched for. The IR spectrum of [$SnBr_4(Me_2SO)_2$] suggests a *cis*-octahedral molecular structure with the Me_2SO ligands coordinated to tin through the O atom (Harrison, Lane & Zuckerman, 1972), and its Mössbauer quadrupole splitting agrees within experimental error with those of [*cis*-$SnBr_2Cl_2(Me_2SO)_2$] (Tudela, Fernández, Tornero & Vegas, 1986) and [*cis*-$SnCl_4(Me_2SO)_2$] (Tudela, Fernández & Tornero, 1985) whose crystal structures have been recently reported (Tudela *et al.*, 1986; Kisenyi, Willey & Drew, 1985). The crystal structure of the title compound has been determined for structural comparison with [$SnCl_4(Me_2SO)_2$] and [$SnBr_2Cl_2(Me_2SO)_2$]. Particular attention is paid to problems arising from pseudosymmetry which affect the three structures to different degrees and had so far not been resolved.

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* ($Å^2 \times 10^4$) *with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3$ (valid within limits of error), $\sigma(U_{eq})$ evaluated using eq. (2) from Schomaker & Marsh (1983).

	x	y	z	U_{eq}
Sn	0·4978 (3)	0·3460 (1)	0·7679 (1)	423 (4)
Br(1)	0·2838 (4)	0·3365 (2)	0·9056 (2)	821 (10)
Br(2)	0·7110 (4)	0·3314 (2)	0·6291 (2)	792 (9)
Br(3)	0·6667 (4)	0·4741 (2)	0·8484 (2)	705 (9)
Br(4)	0·2932 (4)	0·4434 (2)	0·6638 (2)	694 (9)
S(1)	0·7082 (9)	0·1638 (5)	0·8259 (6)	748 (23)
S(2)	0·3307 (9)	0·2028 (4)	0·6129 (5)	605 (21)
O(1)	0·6517 (20)	0·2552 (9)	0·8640 (12)	664 (52)
O(2)	0·3759 (19)	0·2224 (10)	0·7173 (11)	651 (50)
C(3)	0·9144 (27)	0·1580 (19)	0·8785 (19)	816 (89)
C(4)	0·5852 (37)	0·0867 (16)	0·9007 (20)	833 (103)
C(5)	0·4178 (34)	0·0953 (17)	0·5909 (20)	923 (118)
C(6)	0·1154 (30)	0·1726 (21)	0·6160 (17)	771 (97)

Table 2. *Bond lengths* (Å) *and angles* (°)

Sn—Br(1)	2·535 (4)	S(1)—O(1)	1·507 (13)
Sn—Br(2)	2·549 (4)	S(2)—O(2)	1·487 (13)
Sn—Br(3)	2·531 (3)	S(1)—C(3)	1·745 (21)
Sn—Br(4)	2·549 (3)	S(1)—C(4)	1·809 (23)
Sn—O(1)	2·205 (15)	S(2)—C(5)	1·745 (23)
Sn—O(2)	2·153 (15)	S(2)—C(6)	1·732 (23)
Br(1)—Sn—Br(2)	172·0 (1)	O(1)—Sn—O(2)	84·9 (5)
Br(1)—Sn—Br(3)	93·6 (1)	Sn—O(1)—S(1)	119·4 (9)
Br(1)—Sn—Br(4)	91·8 (1)	Sn—O(2)—S(2)	124·3 (9)
Br(2)—Sn—Br(3)	92·6 (1)	O(1)—S(1)—C(3)	100 (1)
Br(2)—Sn—Br(4)	92·4 (1)	O(1)—S(1)—C(4)	102 (1)
Br(3)—Sn—Br(4)	97·9 (1)	C(3)—S(1)—C(4)	103 (1)
Br(1)—Sn—O(1)	83·3 (4)	O(2)—S(2)—C(5)	105 (1)
Br(2)—Sn—O(1)	92·1 (4)	O(2)—S(2)—C(6)	104 (1)
Br(3)—Sn—O(1)	85·4 (4)	C(5)—S(2)—C(6)	99 (1)
Br(4)—Sn—O(1)	174·3 (5)		
Br(1)—Sn—O(2)	84·3 (4)		
Br(2)—Sn—O(2)	88·8 (4)		
Br(3)—Sn—O(2)	170·3 (4)		
Br(4)—Sn—O(2)	91·6 (4)		

Experimental. Crystals from recrystallization in acetonitrile. D_m measured by flotation in $CHBr_3$–CCl_4. Crystals selected using the polarizing microscope and precession photographs. Crystal fragment 0·11 × 0·08 × 0·13 mm with approximately prismatic shape (basal planes {010} well developed) mounted in a Lindemann-glass capillary on a CAD-4 automatic single-crystal diffractometer, with φ axis nearly ‖ **c**. Mo $K\alpha$ radiation in combination with a flat graphite monochromator. Unit-cell parameters from least-squares refinement of 137 measurements on 50 reflections in the range $16·70 \leq 2\theta \leq 48·20°$. Intensity data from ω scan at $\psi = 0$ over a width of $\Delta\omega = 1·10°$, scan time 24 s per reflection, and background for 6 s at either side. Two reference reflections ($22\bar{5}$, $\bar{2}\bar{2}\bar{5}$) were checked every 2 h for intensity and every 100 reflections for orientation, showing an intensity variation within ±5% ($\sigma I/I = 0·8\%$ for the mean) and orientation variations less than 0·15°. Total of 4835 different reflections measured, with $2 \leq \theta \leq 30°$ and $-10 \leq h \leq 10$, $0 \leq k \leq 20$, $0 \leq l \leq 19$ except for the reference reflections. Background and polarization correction to obtain 4835 observed structure amplitudes $F_o(hkl)$. $\langle\sigma F/F\rangle = 0·048$ for 1308 reflections with $F > 6\sigma F$ among which 1260 are unique in $P2_1/n$. Starting positions in $P2_1/n$ (all atoms except H) from Kisenyi *et al.* (1985) and Tudela *et al.* (1986). Scattering factors and dispersion corrections for neutral atoms from Cromer & Waber (1965) and Cromer & Liberman (1970). Isotropic full-matrix least-squares refinement (F magnitudes; program *SHELX76*, Sheldrick, 1976) converged to $R = 0·137$, $wR = 0·094$ for 53 parameters. At this stage, an empirical absorption correction was applied using program *DIFABS* of Walker & Stuart (1983). Correction factors were between 0·588 and 1·168, the residual dropped from 0·134 to 0·114. Further refinement, allowing for anisotropic motion and including H bonded to C as rigid groups [$U_{iso} = 0·1315(253)$ $Å^2$], converged to $R = 0·076$, $wR = 0·047$, $S = 2·34$ for 131 parameters and weight = $1/\sigma^2$. Last shifts $< 0·5\sigma$ except for the orientation of the methyl group $C(5)H_3$ with $1·3\sigma$. Final difference Fourier map showed min./max. of $-1·41/1·66$ e $Å^{-3}$, which is about $\frac{1}{4}$ in height of the weakest C atom. Better agreement was not achieved due to pseudosymmetry problems which will be reported below in a separate section.

Discussion. Atomic parameters and bond distances and angles are given in Tables 1 and 2.* A perspective view of the molecule with the labelling scheme is shown in Fig. 1.

The title compound is isomorphous with $[SnCl_4(Me_2SO)_2]$ (Kisenyi *et al.*, 1985) and displays the same slightly distorted octahedral coordination

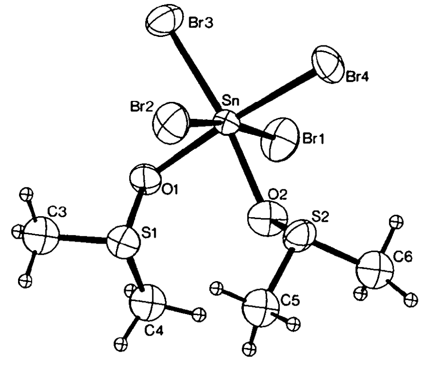

Fig. 1. Molecular structure of $[SnBr_4(Me_2SO)_2]$ with labelling scheme.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52265 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

around Sn with the two Me_2SO ligands bonded through O in *cis* position. The O(1)—Sn—O(2) angle for $[SnBr_4(Me_2SO)_2]$ [84·9 (5)°] is slightly larger than that for $[SnCl_4(Me_2SO)_2]$ [83·26 (30)°]. This is opposed to the trend expected from Zahrobsky's (1971) stereochemical model and suggests that factors other than non-bonded interactions also play a fundamental role in determining the molecular geometry. The average Sn—O distance for $[SnBr_4(Me_2SO)_2]$ is longer than that for $[SnCl_4(Me_2SO)_2]$ [2·179 (15) *vs* 2·110 (7) Å] and the average S—O distance shorter [1·497 (14) *vs* 1·558 (8) Å], showing a weaker Sn—ligand bond consistent with the lower electronegativity of Br. The Sn—Br bond distances do not distinguish between Br atoms *cis* and *trans* to the Me_2SO ligands, and the average Sn—Br distance [2·536 (4) Å] is in the range reported for $SnBr_4$ complexes, from 2·514 (3) Å for $[SnBr_4(C_{10}H_{20}N_2O_2)(C_4H_8O)]$ (Claire, Willey & Drew, 1987) to 2·563 (13) Å for $[SnBr_4(C_5H_{12}N_2O)_2]$ (Calogero, Russo, Valle, Barnard & Donaldson, 1982). The geometry of the dimethyl sulfoxide ligand is similar to other O-coordinated Me_2SO complexes (Davies, 1981). In the mixed halide compound $[SnBr_2Cl_2(Me_2SO)_2]$ (Tudela *et al.*, 1986) the average values of the Sn—halide and Sn—O bond distances fall about midway between those for $[SnCl_4(Me_2SO)_2]$ and $[SnBr_4(Me_2SO)_2]$.

Pseudosymmetry

The packing of $[SnBr_4(Me_2SO)_2]$ molecules is shown in Fig. 2. It consists of layers $\perp \mathbf{c}_m$ of molecules *A* and *B* which are related by a twofold screw axis. A second layer, containing molecules *C* and *D*, is related to the first by an inversion centre.

Problems with symmetry in the structures $[SnX_4(Me_2SO)_2]$, X = Cl, Br, were first reported for $[SnBr_2Cl_2(Me_2SO)_2]$ where the molecules, which exhibit the same geometry as in $[SnBr_4(Me_2SO)_2]$, were found to occupy statistically two alternative orientations (Tudela *et al.*, 1986). This structure has been refined in the triclinic space group $P\bar{1}$ but, for comparison with $[SnBr_4(Me_2SO)_2]$, it is convenient to define a metrically monoclinic unit cell using the vector set $\mathbf{a}_t$, $-\mathbf{a}_t-2\mathbf{c}_t$, $\mathbf{b}_t$. The new cell (a_m = 7·524, b_m = 14·577, c_m = 13·506 Å, α_m = 90·00, β_m = 90·83, γ_m = 89·99°, space group $C\bar{1}$) is isomorphous to that of $[SnBr_4(Me_2SO)_2]$ and, as seen from Fig. 2, the structures would match except for the symmetry element which relates molecules *A* and *B* (or *C* and *D*) within one layer: $C\bar{1}$ imposes a translation instead of the screw axis in $P2_1/n$. Thus, in the general case, the two space groups imply different packing. For $[SnBr_2Cl_2(Me_2SO)_2]$, however, it can easily be shown that the atomic coordinates (transformation to monoclinic setting: $x_m = x_t - 0{\cdot}5z_t - 0{\cdot}25$, $y_m = -0{\cdot}5z_t + 0{\cdot}25$, $z_m = y_t$) comply, within the limits of error ($\Delta < 3\sigma_\Delta$), also with space group $P2_1/n$ as well as with the common supergroup $C2/c$. That means that two orientations, *e.g.* B_m and B_t in Fig. 2, are simultaneously present at each site, and no *a priori* distinction between the $C\bar{1}$ or $P2_1/n$ packing mode can be made.

For the title compound, precession photographs $\perp$ **a** and $\perp$ **b** showed diffraction symmetry $2/mP-2_1/n-$, but strong reflections comply with the additional condition hkl: $h+k=2n$ suggesting $2/mC-c-$ as a possible pseudosymmetry. A quantitative analysis of diffraction symmetry (program *DIFRASYM*; Gregorkiewitz, Vezzalini & Alberti, 1987) showed that $P-2_1/n-$ is the most probable space group (residual error of space group $R_{s,t}$ = 0·036), but the presence of many weak $h0l$: $h+l\neq 2n$ reflections with $I \leq 4{\cdot}2\sigma I$ indicates a small deviation from glide plane $-n-$. This may be due either to the presence of some region with $C\bar{1}$ packing, or because the real symmetry of $[SnBr_4(Me_2SO)_2]$ corresponds to space group $P2_1$ or $P\bar{1}$ as subgroups of $P2_1/n$ (systematic absences on $0k0$: $k = 2n+1$ are obeyed within $I \leq 1{\cdot}3\sigma I_o$).

In order to test these hypotheses, additional refinements in the possible super- and subgroup symmetries were performed. Refinement in $C2/c$ converges to R = 0·094 for 691 unique reflections (R = 0·40 for 1260 reflections) and gives an average model

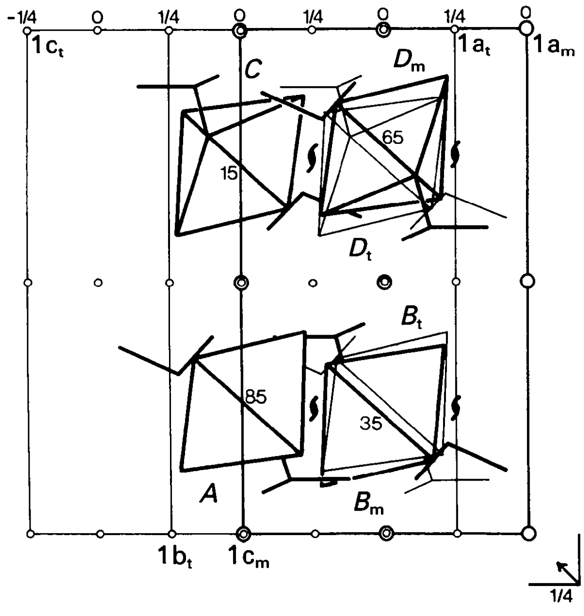

Fig. 2. Packing of $[SnBr_4(Me_2SO)_2]$ molecules in the monoclinic unit cell $P2_1/n$ (heavy drawing). Light drawings refer to triclinic cell which is isomorphous to that of $[SnBr_2Cl_2(Me_2SO)_2]$ (see text). Molecules *A* and *C* are common to both cells, molecules *B* and *D* are obtained by applying a twofold screw in the monoclinic cell and the translation ($+\mathbf{c}_t+\mathbf{a}_t$) in the triclinic one. Heights refer to the monoclinic setting.

simulating superposition of two orientations of the molecule as discussed above for $[\mathrm{SnBr_2Cl_2(Me_2SO)_2}]$. Refinements in $P2_1$ and $P\overline{1}$, starting with the model in $P2_1/n$, show bad convergence and give no significant (Hamilton, 1965) changes. In both subgroups, tests were also made for several alternatives with respect to the molecular orientation, but they show considerably higher residual errors ($R \approx 0{\cdot}10$–$0{\cdot}12$).

In view of these results, essential deviations from the model in $P2_1/n$ towards one of its subgroups are improbable, and the observed incongruencies (small deviation from $-n-$, small difference Fourier map maxima corresponding to the alternative molecular orientation, *e.g.* B_t in Fig. 2) are more likely due to a domain structure involving the pseudosymmetry $C2/c$. One possibility would be the accidental replacement of the 2_1 screw by the centring operation $(\frac{1}{2}+,\frac{1}{2}+,0)$ for packing of adjacent molecules, *e.g.* A and B in Fig. 2. It seems plausible that the tendency for this mistake is greater for the title compound than for its Cl analogue, where the organic ligands play a more important role in determining the packing. A similar model might also apply to the packing of $[\mathrm{SnBr_2Cl_2(Me_2SO)_2}]$, where the symmetry indetermination is greatest due to the Cl–Br substitutional disorder.

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Structure of $[\mathrm{Ni(Me_8[14]ane}C\alpha)](\mathrm{ClO_4})_2$ ($\mathrm{Me_8[14]ane}$ = 2,5,5,7,9,12,12,14-Octamethyl-1,4,8,11-tetraazacyclotetradecane)

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Abstract. $[\mathrm{Ni(C_{18}H_{40}N_4)}](\mathrm{ClO_4})_2$, $M_r = 570{\cdot}2$, monoclinic, $P2_1/n$, $a = 10{\cdot}222\,(2)$, $b = 8{\cdot}741\,(1)$, $c = 14{\cdot}495\,(3)$ Å, $\beta = 99{\cdot}60\,(2)°$, $V = 1277{\cdot}1\,(7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}48$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 10{\cdot}2$ cm^{-1}, room temperature, $R = 0{\cdot}042$ for 1916 observed reflections. The nickel(II) complex contains a centrosymmetric cation with square planar nickel and Ni—N distances 1·961 (2) and 1·948 (3) Å; the configuration at the chiral nitrogen centres is *RSSR* or *SRRS*. The perchlorate anion is disordered over two sites and is hydrogen bonded to the N—H groups of the cation, with N···O distances 2·99 to 3·20 Å.

Introduction. 1,2-Propanediamine reacts (Curtis, Swann, Waters & Maxwell, 1969) with acetone to

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