Preparation of the Sixteen-atom Ring Chelates *trans*-[$M_2Cl_4\{Bu^tS(CH_2)_5SBu^t\}_2$], M = Pd or Pt: Crystal Structure of *trans*-[$Pd_2Cl_4\{Bu^tS(CH_2)_5SBu^t\}_2$] †

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Treatment of [$PdCl_2(NCPh)_2$] or [$PtCl_2(NCBu^t)_2$] with the new disulphide $Bu^tS(CH_2)_5SBu^t$ gives 16-atom ring chelates of the type *trans*-[$M_2Cl_4\{Bu^tS(CH_2)_5SBu^t\}_2$]. Crystals of the compound with M = Pd are monoclinic, space group $P2_1/n$, with a = 17.359(4), b = 11.278(4), c = 23.080(6) Å, β = 101.19(2)°, and Z = 4. The 16-membered ring is rectangular with the bulky Bu^tS groups forming the four corners, and it has the elongated-boat or ' barge ' conformation.

We have shown that sterically demanding substituents on phosphorus or nitrogen donor atoms are very effective in stabilizing large chelate rings relative to open-chain structures.[1-4] Compounds which suitably illustrate the phenomenon are the 16-atom rings of [$Pd_2Cl_4\{Me_2N(CH_2)_nNMe_2\}_2$] and [$Pd_2Cl_4\{Bu^t{}_2P(CH_2)_nPBu^t{}_2\}_2$] ($n = 5$) and the corresponding 20-atom rings ($n = 7$). All four complexes have had their crystal structures determined by X-ray diffraction.[2-4] Thus the 16-atom ring in [$Pd_2Cl_4\{Me_2N(CH_2)_5NMe_2\}_2$] adopts the ' sofa ' conformation (C_{2h}) with the mutually *trans* NMe_2 groups staggered: the Pd–N–CH_2–CH_2 torsion angles are close to 60°, *i.e.* the NMe_2 groups occupy ' corner ' positions.[3] Each Cl–Pd–Cl group is approximately vertical to the plane of the four nitrogens. In this way the chlorines are at maximum distance from the inward-pointing pseudo-equatorial hydrogens of the β-methylenes. Space-filling molecular models suggest that repulsion between the chlorines and the hydrogens of the methyl groups (*i.e.* α-hydrogens) is less important and each chlorine is eclipsed with one methyl group.

In contrast the 16-atom ring in [$Pd_2Cl_4\{Bu^t{}_2P(CH_2)_5PBu^t{}_2\}_2$] adopts the ' barge ' conformation (C_{2v}) with the Pd–P–CH_2–CH_2 torsion angles close to 60°. The mutually *trans* $PBu^t{}_2$ groups are eclipsed probably to minimize interactions with the Cl–Pd–Cl moiety, hence the ' barge ' conformation of the ring.[2-4]

Sulphur in dialkyl sulphides has a similar radius to phosphorus in tertiary phosphines and we reasoned that a disulphide such as $Bu^tS(CH_2)_5SBu^t$ ought to form a similar large-ring chelate with palladium, *i.e.* favourable conformational (enthalpy) and entropy effects, induced by the sterically demanding substituents (*i.e.* Bu^t) on the sulphur donor atoms, would operate. In this note we report our results. The long-chain disulphide $PhS(CH_2)_{12}SPh$ gives *trans*-chelate complexes, *trans*-[MX_2L] (M = Pd or Pt; X = Cl or Br) containing a large chelate ring (15-membered).[5,6] None of these complexes has had its crystal structure determined.

RESULTS AND DISCUSSION

The disulphide $Bu^tS(CH_2)_5SBu^t$ was readily prepared by the action of sodium t-butyl sulphide on 1,5-dibromopentane in a benzene–water two-phase system using a phase-transfer catalyst. The product was not obtained analytically pure (Found: C, 61.05; H, 10.7. $C_{13}H_{28}S_2$ requires C, 62.85; H, 11.35%) but was sufficiently pure for our purposes. Its ^1H n.m.r. spectrum showed resonances of the expected intensity ratio 4 : 6 : 18, corresponding to SCH_2, $CH_2CH_2CH_2CH_2$, and Bu^t respectively, and the mass spectrum showed a parent molecular ion at the expected m/e value (248). Treatment of [$PdCl_2(NCPh)_2$] with $Bu^tS(CH_2)_5SBu^t$ in toluene gave a yellow precipitate which on heating gradually dissolved. The expected binuclear complex, [$Pd_2Cl_4\{Bu^tS(CH_2)_5SBu^t\}_2$], was isolated from the solution as yellow microcrystals in good (65%) yield. The structure is discussed below. We could find no evidence for a cyclometallated complex such as is formed from $Bu^t{}_2P(CH_2)_5PBu^t{}_2$ and palladium(II) chloride in addition to the large chelate ring.[2] Treatment of [$PtCl_2(NCBu^t)_2$] with $Bu^tS(CH_2)_5SBu^t$ in toluene gave the corresponding platinum complex, [$Pt_2Cl_4\{Bu^tS(CH_2)_5SBu^t\}_2$]·$C_7H_8$, in 79% yield. The i.r. spectrum of this complex over the range 400—4 000 cm^{-1} was virtually identical to that of the palladium complex and it clearly has an analogous structure.

Crystal Structure of [$Pd_2Cl_4\{Bu^tS(CH_2)_5SBu^t\}_2$].—The molecular structure is shown in the Figure and selected bond lengths and angles are given in Table 1. The 16-membered ring is seen to be of rectangular shape, with sides formed by the extended S–$(CH_2)_5$–S chains and by the *trans* S–Pd–S linkages, while the bulky Bu^tS groups form the four corners. This is very similar to the structure found for the 20-membered ring phosphine complex

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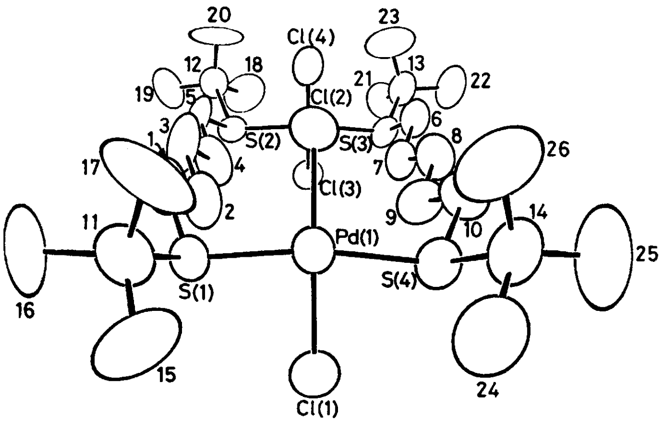
†Bis(μ-1,5-di-t-butylthiopentane-*SS′*)-bis[dichloropalladium(II)].

$[Pd_2Cl_4\{Bu^t{}_2P(CH_2)_7PBu^t{}_2\}_2]$ [2,4] and as in that compound the disulphide complex has an elongated-boat or ' barge ' conformation. This conformation is preferred because it allows all of the Cl–Pd–S–Bu^t torsion angles to be *ca.* 90°, thereby minimizing the Cl · · · Bu^t steric interactions, whereas the alternative elongated-chair (' sofa ') conformation does not. In fact the four Cl–Pd–S–Bu^t torsion angles involving the inward-pointing chlorines Cl(2) and Cl(4) are 79—86° (mean 82°) while the four involving the outward-pointing chlorines Cl(1) and Cl(3) are 93—102° (mean 98°); these 8° departures from 90° result from the additional interaction between the inward-pointing chlorines and the α-methylene groups of the $-(CH_2)_5-$ chains.



ORTEP drawing showing the molecular structure and atom numbering; atom Pd(2) is obscured by atom Cl(2). Carbon atoms bear numbers only

TABLE 1

Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Pd(1)–S(1)	2.322(5)	Pd(2)–S(2)	2.307(5)
Pd(1)–S(4)	2.348(6)	Pd(2)–S(3)	2.338(5)
Pd(1)–Cl(1)	2.313(7)	Pd(2)–Cl(3)	2.302(7)
Pd(1)–Cl(2)	2.278(6)	Pd(2)–Cl(4)	2.303(7)
S(1)–C(1)	1.78(3)	S(3)–C(6)	1.77(2)
S(1)–C(11)	1.87(3)	S(3)–C(13)	1.86(3)
S(2)–C(5)	1.80(2)	S(4)–C(10)	1.80(3)
S(2)–C(12)	1.89(2)	S(4)–C(14)	1.92(3)
S(1)–Pd(1)–S(4)	168.8(2)	S(2)–Pd(2)–S(3)	171.8(2)
Cl(1)–Pd(1)–Cl(2)	179.2(2)	Cl(3)–Pd(2)–Cl(4)	179.2(2)

EXPERIMENTAL

The general preparative and spectroscopic techniques were the same as those described in other recent papers from this laboratory.[7] Methyltrialkyl(C_8—C_{10})ammonium chloride (ADOGEN-464) was purchased from Aldrich.

1,5-*Di(t-butylthio)pentane*.—1,1-Dimethylethanethiol (4.5 g, 50 mmol) was added to a mixture of a solution of sodium hydroxide (3.5 g, 87 mmol) and methyltrialkyl(C_8—C_{10})-ammonium chloride (0.4 g) in degassed water (50 cm^3) and 1,5-dibromopentane (4.75 g, 25 mmol) in degassed benzene (40 cm^3). The mixture was stirred vigorously for 90 min then refluxed with stirring for 30 min, all under nitrogen. The organic layer was isolated, dried (Mg[SO_4]), and distilled to give the required product as a colourless oil, b.p. 105 °C (4×10^{-3} mmHg).* Yield 4.7 g (75%).

trans-$[Pd_2Cl_4\{Bu^tS(CH_2)_5SBu^t\}_2]\cdot C_7H_8$.—A mixture of $[PdCl_2(NCPh)_2]$ (0.414 g, 1.08 mmol) and $Bu^tS(CH_2)_5SBu^t$ (0.258 g, 1.03 mmol) was stirred in toluene (20 cm^3). The solids rapidly dissolved to give an orange solution and after *ca.* 2 min a yellow precipitate formed. The mixture was heated under reflux for 90 min during which the solid dissolved. The solution was filtered, evaporated to dryness, and the orange oil triturated with methanol to give the required product as a yellow solid (yield 0.29 g, 65%). It formed orange prisms of the toluene solvate from hot toluene (Found: C, 42.4; H, 7.05; Cl, 15.2; S, 13.75. $C_{33}H_{64}Cl_4Pd_2S_4$ requires C, 42.0; H, 6.85; Cl, 15.0; S, 13.6%).

trans-$[Pt_2Cl_4\{Bu^tS(CH_2)_5SBu^t\}_2]\cdot C_7H_8$.—A solution of $Bu^tS(CH_2)_5SBu^t$ (0.29 g, 1.15 mmol) in toluene (10 cm^3) was added to a solution of $[PtCl_2(NCBu^t)_2]$ (0.47 g, 1.1 mmol) in toluene (10 cm^3) with stirring. The mixture was then heated under reflux for 35 min and filtered. The filtrate was evaporated and hexane added to the residue. The required product separated as yellow prisms. Yield 0.45 g (79%). It formed yellow *prisms* from toluene of the toluene solvate (Found: C, 35.4; H, 5.7; Cl, 12.35; S, 11.65. $C_{33}H_{64}Cl_4Pt_2S_4$ requires C, 35.35, H, 5.25; Cl, 12.65; S, 11.45%).

TABLE 2

Atomic co-ordinates with estimated standard deviations in parentheses

Pd(1)	0.536 16(10)	0.386 02(16)	0.252 11(7)
Pd(2)	0.213 94(10)	0.403 38(15)	0.447 26(7)
S(1)	0.443 4(3)	0.457 8(5)	0.173 7(2)
S(2)	0.119 7(3)	0.469 3(5)	0.369 3(3)
S(3)	0.309 9(3)	0.364 6(6)	0.531 2(3)
S(4)	0.635 6(4)	0.352 8(6)	0.335 2(3)
Cl(1)	0.607 5(4)	0.555 2(6)	0.241 6(3)
Cl(2)	0.467 5(4)	0.218 1(5)	0.263 0(3)
Cl(3)	0.193 7(4)	0.579 7(5)	0.492 3(3)
Cl(4)	0.234 9(4)	0.228 4(6)	0.401 2(3)
C(1)	0.350 0(14)	0.399 0(23)	0.178 8(9)
C(2)	0.328 1(15)	0.467 2(29)	0.234 9(10)
C(3)	0.242 8(13)	0.404 4(31)	0.238 5(10)
C(4)	0.219 0(18)	0.472 9(27)	0.295 3(10)
C(5)	0.140 5(11)	0.412 6(23)	0.301 0(8)
C(6)	0.382 9(12)	0.275 3(22)	0.509 6(9)
C(7)	0.421 0(14)	0.351 1(22)	0.467 9(10)
C(8)	0.491 9(14)	0.286 9(23)	0.450 7(9)
C(9)	0.528 4(15)	0.351 9(24)	0.408 5(11)
C(10)	0.596 0(14)	0.273 5(22)	0.390 7(11)
C(11)	0.465 9(15)	0.391 8(20)	0.104 7(10)
C(12)	0.023 4(11)	0.393 2(22)	0.371 2(11)
C(13)	0.267 6(14)	0.266 1(24)	0.581 6(10)
C(14)	0.712 9(13)	0.241 5(22)	0.319 7(11)
C(15)	0.538 9(15)	0.454 1(30)	0.095 2(12)
C(16)	0.391 3(17)	0.434 3(33)	0.052 5(10)
C(17)	0.477 0(22)	0.258 0(22)	0.109 5(13)
C(18)	0.012 9(17)	0.432 8(35)	0.436 9(15)
C(19)	−0.033 8(16)	0.445 4(30)	0.322 5(14)
C(20)	0.027 7(19)	0.260 9(23)	0.359 3(19)
C(21)	0.207 3(17)	0.340 1(27)	0.603 8(12)
C(22)	0.334 0(16)	0.223 1(30)	0.629 5(11)
C(23)	0.233 8(20)	0.155 7(27)	0.548 9(13)
C(24)	0.747 2(15)	0.315 1(29)	0.272 2(13)
C(25)	0.768 8(18)	0.221 0(32)	0.374 8(12)
C(26)	0.673 4(17)	0.127 6(26)	0.292 1(16)

Crystal Data.—$[Pd_2Cl_4\{Bu^tS(CH_2)_5SBu^t\}_2]\cdot C_7H_8$, $C_{33}H_{64}Cl_4Pd_2S_4$, $M = 943.7$, Monoclinic, $a = 17.359(4)$, $b = 11.278(4)$, $c = 23.080(6)$ Å, $\beta = 101.19(2)°$, $U = 4\,433(2)$ Å^3, $Z = 4$, $D_c = 1.414$ g cm^{-3}, $F(000) = 1\,944$, space group

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* Throughout this Note: 1 mmHg ≈ 13.6 × 9.8 Pa.

$P2_1/n$. Mo-K_α radiation, graphite monochromatized, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 12.45 cm^{-1}.

Structure Determination.—Cell dimensions were determined by least-squares treatment of the diffractometer angles of 15 reflections having $35 < 2\theta < 40°$. Intensities of all independent reflections having $4 < 2\theta < 45°$ were measured in the θ—2θ scan mode, and the structure analysis used the 3 408 intensities with $I > 3\sigma(I)$. There was a *ca*. 30% fall in the intensity of a control reflection during the course of data collection, but because this was possibly caused by a loss of toluene from the crystal, not necessarily accompanied by complete decomposition, a correction for the decay was not applied. After correction for Lorentz, polarization, and transmission factors, and solution of the structure from Patterson and electron-density syntheses, least-squares refinement with anisotropic temperature factors converged at $R = 0.095$ and $R' = 0.145$. Hydrogen atoms and the toluene carbon atoms were not included in the refinement. In a final difference synthesis the toluene molecule appeared as a disc of electron density centred at approximately (0.1, 0.3, 0.1), but without individual atoms clearly resolved. Atomic scattering factors were taken from ref. 8 and weights were derived from the modified variances $\sigma^2(I) = \sigma_c^2(I) + (0.07I)^2$, σ_c^2 being the variance obtained from counting statistics. The atomic co-ordinates and their estimated standard deviations are given in Table 2. Vibrational parameters and observed and calculated structure factors are listed in Supplementary Publication No. SUP 22844 (23 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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