Formation of Large Chelate Rings from *NNN'N'*-Tetramethyl-pentane-1,5-diamine, -heptane-1,7-diamine, and -decane-1,10-diamine and Bis(benzonitrile)dichloropalladium(II): Crystal Structures of Di-μ-(*NNN'N'*-tetramethylpentane-1,5-diamine-*NN'*)- and Di-μ-(*NNN'N'*-tetramethylheptane-1,7-diamine-*NN'*)-bis[dichloropalladium(II)]–Benzene (1/1) containing Sixteen- and Twenty-atom Rings respectively†

By **Anthony Constable, Walter S. McDonald,*** and **Bernard L. Shaw,*** School of Chemistry, The University, Leeds LS2 9JT

Treatment of $[PdCl_2(NCPh)_2]$ with $Me_2N[CH_2]_nNMe_2$ (n = 5, 7, or 10) gives binuclear complexes *trans*-$[Pd_2Cl_4\{Me_2N(CH_2)_nNMe_2\}_2]$ in good yield. The crystal structures of the 16-atom ring (n = 5) and 20-atom ring (n = 7) complexes were determined from 2577 and 1154 diffractometer data, respectively, and were refined to R of 0.034 and 0.057, respectively. They are compared with the structures of *trans*-$[Pd_2Cl_4\{Bu^t{}_2P(CH_2)_nPBu^t{}_2\}_2]$ (n = 5 or 7). The rings in the amine complexes adopt an elongated-chair ('sofa') conformation whilst those of the phosphine complexes have an elongated-boat ('barge') conformation. Factors affecting the conformations and stabilities of these large chelate rings are discussed. Crystal data are: $[Pd_2Cl_4\{Me_2N(CH_2)_5NMe_2\}_2]\cdot C_6H_6$, space group $P\bar{1}$, $Z = 1$, $a = 8.425(2)$, $b = 12.624(2)$, $c = 8.217(2)$ Å, $\alpha = 105.16(2)$, $\beta = 98.12(2)$, $\gamma = 71.83(2)°$; $[Pd_2Cl_4\{Me_2N(CH_2)_7NMe_2\}_2]\cdot C_6H_6$, space group $Cmca$, $Z = 4$, $a = 29.387(4)$, $b = 8.030(2)$, $c = 15.177(3)$ Å.

UNTIL recently very few large-ring chelates (> eight membered rings), formed from flexible bidentate ligands, had been described. Ligands of the type $A[CH_2]_nA'$ where $n \geqslant 5$ and A and A' are donor groups tend to bridge metal atoms (ions) in preference to forming a chelate ring. The effect of increasing ring size on the relative stabilities of open-chain and chelate structures has been discussed in several papers, books, and reviews.[1-7] However, we and other workers have successfully made large chelate-ring compounds (12—72-membered).[8-16] Some of these compounds may have been formed under conditions of kinetic control, others require high-dilution techniques for synthesis, *e.g.* complexes of the type *trans*-$[PtCl_2\{CH_2{=}CH(CH_2)_mCO_2(CH_2)_nC_5H_2Me_2N\}]$ which undergo slow polymerization when in concentrated solution.[13] However, for complexes of tetra-t-butyldiphosphines $Bu^t{}_2P[CH_2]_nPBu^t{}_2$ (n = 5—10 or 12) large-ring chelate complexes are formed and these are more thermodynamically stable than open-chain complexes. For example, we have heated toluene solutions of the large-ring complexes $[PtCl_2\{Bu^t{}_2P(CH_2)_{10}PBu^t{}_2\}]$ or $[Pt_2Cl_4\{Bu^t{}_2P(CH_2)_{10}PBu^t{}_2\}_2]$ at 135 °C for several weeks and although we observed interconversion of the 13- and 26-membered ring complexes we could not detect any open-chain species by ^{31}P n.m.r. spectroscopy.[17] The effect of the bulky $PBu^t{}_2$ end groups in stabilizing these large rings has been explained in terms of favourable torsional (conformational) enthalpy effects, and also a favourable effect on the entropy of chelate-ring formation.[18]

The analogy between the effect of methyl substituents on carbon in promoting ring formation, *e.g.* the Thorpe–Ingold or *gem*-dimethyl effect of organic chemistry and our *gem*-t-butyl effect, has been pointed out previously.[19] More recently[18] we have compared effects operating in our chelate complexes with the effects of methyl substituents in determining the relative stabilities of cyclic monomers and open-chain polymers.[20] Dale[21] and Anet and Anet[22] have discussed the effects of *gem*-dimethyl substituents on the conformations and stabilities of large carbocyclic rings. *gem*-Dimethyl substituents occupy 'corner positions' in for example 1,1-dimethylcyclodecane. Since sp^3-hybridized nitrogen is smaller than sp^3-hybridized carbon we reasoned that *gem*-dimethyl substituents on a nitrogen donor atom would also preferentially occupy 'corner positions' (in chelate complexes), *i.e.* a ligand of type $Me_2N[CH_2]_nNMe_2$ would be better at forming large chelate rings than the corresponding primary diamine, $H_2N[CH_2]_nNH_2$. We have found this to be the case. We have chosen to study the effects of these ligands on palladium(II) chlorides since such systems would be expected to reach equilibrium rapidly when subjected to nucleophilic attack. We also wished to compare the products with the series of chelate-ring complexes of type $[Pd_2Cl_4\{Bu^t{}_2P(CH_2)_nPBu^t{}_2\}_2]$ (n = 5, 7, or 10), the crystal structures of which we have determined.[9,18]

RESULTS AND DISCUSSION

Addition of $H_2N[CH_2]_5NH_2$ to a dichloromethane solution of $[PdCl_2(NCPh)_2]$ gave a yellow-brown amorphous precipitate, totally insoluble in chloroform and other common solvents, which was probably a mixture containing open-chain polynuclear species. We could find no evidence of complexes with chelate rings. In the early 1900's Tschugaeff[23] and Werner[24] studied the action of $H_2N[CH_2]_5NH_2$ on nickel and cobalt ions but were unable to isolate chelate complexes. For example, with a nickel(II) solution a very intractable and yellow amorphous precipitate was obtained.[23] This contrasted with the behaviour of ethylenediamine and propane-1,3-diamine. We now find, however, that addition of $Me_2N[CH_2]_5NMe_2$ to a dark brown solution of $[PdCl_2(NCPh)_2]$ in dichloromethane rapidly gives an orange solution from which orange-brown crystals of the binuclear complex $[Pd_2Cl_4\{Me_2N(CH_2)_5NMe_2\}_2]$ separate in >60% yield. The complex could be recrystallized from dichloromethane–benzene without apparent decomposition and its solution in deuteriochloroform was

---

† No reprints available.

stable indefinitely. The structure of this 16-atom ring complex has been determined by single-crystal *X*-ray diffraction and is described and discussed below. The complex was also characterized by elemental analysis, and molecular-weight measurements (see Experimental section). In the i.r. spectrum bands at 323s and 343m(sh) cm^{-1} are assigned to ν(Pd–Cl) and in the ^1H n.m.r. spectrum in $CDCl_3$ there is a methyl resonance at δ 2.5 p.p.m. and methylene resonances at 1.0—2.8 p.p.m.

The compounds $Me_2N[CH_2]_nNMe_2$ ($n = 7$ or 10) reacted similarly with a solution of $[PdCl_2(NCPh)_2]$. The complex $[Pd_2Cl_4\{Me_2N(CH_2)_7NMe_2\}_2]$ is formed readily in 85% yield: no other palladium-containing product could be detected. For this complex ν(Pd–Cl) occurs at 351s cm^{-1} (Nujol) and in the ^1H n.m.r. spectrum δ(CH_3) is 2.45, δ(CH_2) 1.1—2.7, and δ(C_6H_6) 7.3 p.p.m. The structure, determined by single-crystal *X*-ray diffraction, is discussed below. The complex $[Pd_2Cl_4\{Me_2N(CH_2)_{10}NMe_2\}_2]$ formed in 41% yield is formulated as a 26-atom ring complex on the basis of microanalytical and molecular-weight data and on the basis of one strong band (at 356 cm^{-1}) due to ν(Pd–Cl): the ^1H n.m.r. resonances at δ 1.18—2.68 p.p.m. were broad.

The complexes $[Pd_2Cl_4\{Me_2N(CH_2)_nNMe_2\}_2]$ ($n = 5$ or 7) crystallized from benzene–CH_2Cl_2 as benzene solvates in which the *X*-ray structure analyses reveal columns of alternating benzene and $[Pd_2Cl_4\{Me_2N(CH_2)_nNMe_2\}_2]$ molecules. Figures 1 and 2 show the molecular structures of the two complexes, with their neighbouring benzene molecules also shown. Table 1 gives the atomic co-ordinates. In the complex with $n = 5$ (Figure 1) the large-ring complex and the benzene molecules alternate along a row of crystallographic symmetry centres.

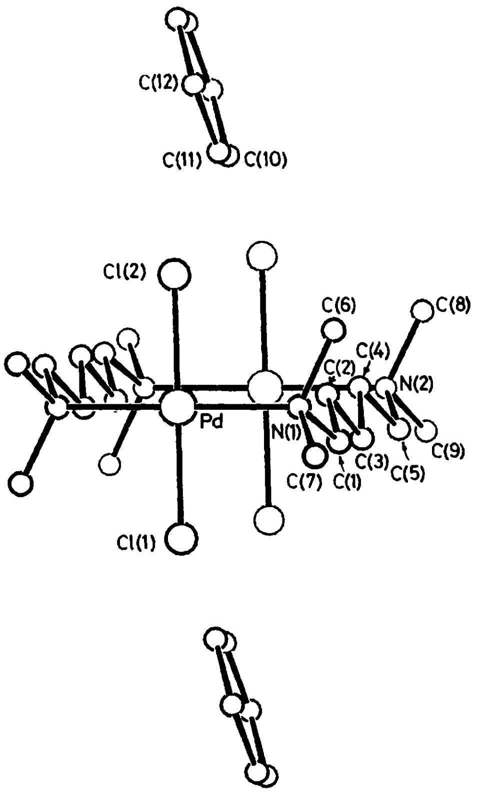


FIGURE 1 ORTEP drawing of $[Pd_2Cl_4\{Me_2N(CH_2)_5NMe_2\}_2]\cdot C_6H_6$, showing the atom numbering. The crystallographically imposed symmetry is C_i

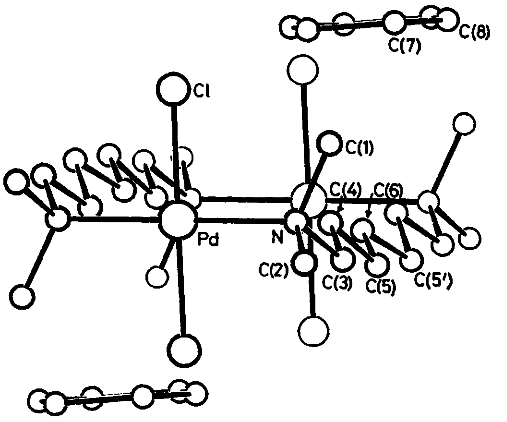


FIGURE 2 ORTEP drawing of $[Pd_2Cl_4\{Me_2N(CH_2)_7NMe_2\}_2]\cdot C_6H_6$, showing the atom numbering. The crystallographically imposed symmetry is C_{2h}

TABLE 1

Atomic co-ordinates with estimated standard deviations in parentheses

	X	*Y*	*Z*
(*a*) $[Pd_2Cl_4\{Me_2N(CH_2)_5NMe_2\}_2]$			
Pd(1)	0.397 2(1)	0.322 5(1)	0.054 5(1)
Cl(1)	0.616 3(1)	0.317 3(1)	0.259 7(1)
Cl(2)	0.178 6(2)	0.325 4(1)	−0.149 8(2)
N(1)	0.234 2(5)	0.349 5(3)	0.247 5(5)
N(2)	0.438 9(5)	−0.291 1(3)	0.140 7(5)
C(1)	0.296 2(7)	0.249 0(4)	0.332 1(6)
C(2)	0.287 9(8)	0.136 8(4)	0.205 5(7)
C(3)	0.379 2(7)	0.034 7(4)	0.288 7(7)
C(4)	0.361 0(8)	−0.077 3(4)	0.166 4(7)
C(5)	0.434 4(7)	−0.176 4(4)	0.257 0(6)
C(6)	0.053 7(7)	0.365 1(5)	0.190 7(9)
C(7)	0.245 2(8)	0.457 1(4)	0.378 0(7)
C(8)	0.263 3(7)	−0.294 1(5)	0.080 5(8)
C(9)	0.509 3(9)	−0.381 4(4)	0.241 6(7)
C(10)	0.906 1(10)	0.055 2(8)	0.375 7(11)
C(11)	0.921 9(10)	−0.059 0(7)	0.356 2(11)
C(12)	1.016 9(11)	−0.114 3(6)	0.482 7(13)
(*b*) $[Pd_2Cl_4\{Me_2N(CH_2)_7NMe_2\}_2]$			
Pd(1)	0.169 0(1)	0.000 0(0)	0.000 0(0)
Cl(1)	0.166 9(1)	0.230 0(3)	−0.090 8(1)
N(1)	0.170 4(3)	0.149 4(9)	0.116 9(4)
C(1)	0.173 7(4)	0.334 9(11)	0.099 4(7)
C(2)	0.213 0(4)	0.110 0(14)	0.166 5(6)
C(3)	0.128 9(4)	0.114 6(14)	0.173 0(6)
C(4)	0.085 0(3)	0.139 1(18)	0.122 0(7)
C(5)	0.043 8(4)	0.097 3(16)	0.181 5(7)
C(7)	0.047 1(9)	0.561 9(29)	0.040 1(16)
C(6)	0.000 0(0)	0.115 7(29)	0.129 3(11)
C(8)	0.000 0(0)	0.606 2(40)	0.073 7(21)

The molecular symmetry closely approximates to C_{2h} which, for the complex with $n = 7$, is the crystallographically imposed symmetry of both complex and benzene molecules. In the latter case the benzene molecules are 'sandwiched' with their planes parallel to the planes of the large-ring chelates, but with the shorter polymethylene chain $-[CH_2]_5-$ the transannular Cl(1) • • • Cl(2′) distance is reduced from 9.8 to 7.6 Å and a similar mutual arrangement of benzene and chelate molecules is not possible. Bond-length, bond-angle, and torsion-angle data for the two complexes are given in Table 2. The conformations of these large-ring complexes contrast with those we have found earlier for the PBu^t_2 analogues.[18] In both types the polymethylene chains have their preferred extended conformations, with NMe_2 or PBu^t_2 occupying ' corner ' positions, as expected. For the PBu^t_2 complexes, however, the two PBu^t_2 groups attached to the same Pd are mutually eclipsed, leading to an elongated boat conformation (1) of C_{2v} symmetry (' barge ' conformation), while the NMe_2 complexes have the NMe_2 groups mutually staggered to give the elongated chair conformation (2) of C_{2h} symmetry (' sofa ' conformation).

TABLE 2

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, and torsion angles (°)

(*a*) $[Pd_2Cl_2\{Me_2N(CH_2)_5NMe_2\}_2]$

Pd–Cl(1)	2.314(1)	Cl(1)–Pd–N(1)	88.5(1)
Pd–Cl(2)	2.308(1)	Cl(1)–Pd–N(2′)	91.7(1)
Pd–N(1)	2.135(4)	Cl(2)–Pd–N(1)	91.3(1)
Pd–N(2′)	2.142(5)	Cl(2)–Pd–N(2′)	88.5(1)
N(1)–C(1)	1.520(7)	N(1)–Pd–N(2′)	178.6(1)
N(1)–C(6)	1.493(7)	Cl(1)–Pd–Cl(2)	179.3(1)
N(1)–C(7)	1.514(6)	Pd–N(1)–C(1)	108.6(3)
C(1)–C(2)	1.538(7)	Pd–N(1)–C(6)	115.6(3)
C(2)–C(3)	1.553(7)	Pd–N(1)–C(7)	107.9(3)
C(3)–C(4)	1.544(7)	Pd′–N(2)–C(5)	108.4(3)
C(4)–C(5)	1.541(8)	Pd′–N(2)–C(8)	115.3(3)
C(5)–N(2)	1.504(6)	Pd′–N(2)–C(9)	108.8(3)
N(2)–C(8)	1.501(8)	N(1)–C(1)–C(2)	110.8(3)
N(2)–C(9)	1.508(8)	C(1)–C(2)–C(3)	108.8(4)
C(10)–C(11)	1.374(14)	C(2)–C(3)–C(4)	109.0(4)
C(11)–C(12)	1.416(13)	C(3)–C(4)–C(5)	108.7(4)
C(12)–C(10′)	1.401(12)	C(4)–C(5)–N(2)	112.2(3)

Torsion angles

Pd–N(1)–C(1)–C(2)	−63	C(2)–C(1)–N(1)–C(6)	64
N(1)–C(1)–C(2)–C(3)	171	C(2)–C(1)–N(1)–C(7)	180
C(1)–C(2)–C(3)–C(4)	176	C(4)–C(5)–N(2)–C(8)	−63
C(3)–C(4)–C(5)–N(2)	−174	C(4)–C(5)–N(2)–C(9)	−179
C(3)–C(4)–C(5)–N(2)	−174		
C(4)–C(5)–N(2)–Pd	63		

(*b*) $[Pd_2Cl_4\{Me_2N(CH_2)_7NMe_2\}_2]$

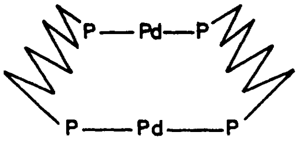
Pd–Cl	2.305(2)	Cl–Pd–N	92.7(2)
Pd–N	2.142(7)	Cl–Pd–N′	87.4(2)
N–C(1)	1.516(12)	N–Pd–N′	177.9(3)
N–C(2)	1.496(14)	Cl–Pd–Cl′	177.0(1)
N–C(3)	1.513(14)	Pd–N–C(1)	114.0(5)
C(3)–C(4)	1.517(16)	Pd–N–C(2)	108.3(5)
C(4)–C(5)	1.548(16)	Pd–N–C(3)	110.4(5)
C(5)–C(6)	1.519(15)	N–C(3)–C(4)	111.9(7)
C(7)–C(8) *	1.52(3)	C(3)–C(4)–C(5)	109.9(8)
C(7)–C(7′) *	1.57(4)	C(4)–C(5)–C(6)	109.7(9)
		C(5)–C(6)–C(5′)	115.8(10)

Torsion angles

Pd–N–C(3)–C(4)	−55	C(4)–C(5)–C(6)–C(5′)	−173
N–C(3)–C(4)–C(5)	178	C(4)–C(3)–N–C(1)	71
C(3)–C(4)–C(5)–C(6)	−178	C(4)–C(3)–N–C(2)	−175

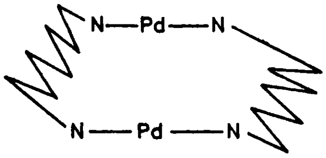
* The atoms of the benzene molecules have high thermal motion and probably some disorder also. Individual molecules are probably displaced in various directions from their crystallographic sites.

The methyl substituents on N or the Bu^t substituents on P may determine the conformation of the ring in two ways. First, if the steric requirements of the Me or Bu^t groups with respect to interaction with the polymethylene chains exceed or are comparable to $PdCl_2$ they will favour the $Pd-XR_2-CH_2-CH_2$ torsion angle of *ca.* 60 rather than 180°, thus assisting cyclization with N or P in a ' corner ' position. Secondly, in the complexes containing PBu^t_2 there is a large energy barrier to rotation of the $PdCl_2$ moiety: one Pd–Cl bond lies between PBu^t_2 groups, which are eclipsed, and the other Pd–Cl bond lies between the inward pointing pseudo-equatorial hydrogen on the β-methylene group and one of the t-butyl groups.[18] In the complexes containing NMe_2 groups, space-filling molecular models suggest that the chlorines would experience the largest repulsion from the pseudo-equatorial hydrogens on the β-methylene groups and to avoid this the Cl–Pd–Cl moiety is approximately at right angles to the ' plane ' of the ring. Moreover, if a ' barge ' conformation were adopted one chlorine would interact equally with two equivalent β-hydrogens whilst the other chlorine would be further away and therefore interact less strongly. Not surprisingly, the ' sofa ' conformation is preferred, for by increasing the N–Pd–Cl angle to >90° (Table 1) each chlorine moves away from the interacting β-hydrogen and from the eclipsing methyl groups. Space-filling molecular models show that interaction of the chlorines with the NMe_2 groups is relatively small (since β-hydrogens are absent).



C_{2v} 'barge' conformation

(1)



C_{2h} 'sofa' conformation

(2)

Preparation of the Diamines.—*NNN′N′*-Tetramethylpentane-1,5-diamine was prepared by the reduction of *NNN′N′*-tetramethylglutaramide with $Li[AlH_4]$. This method is preferable to that described previously,[25] *viz.* decomposition of $[Me_3N(CH_2)_5NMe_3]^{2+}$. *NNN′N′*-Tetramethylheptane-1,7-diamine was prepared by treating the corresponding α,ω-dibromide with dimethylamine, treatment with base, and distillation. This method is preferable to that previously described [26] and is similar to the literature method for *NNN′N′*-tetramethyldecane-1,10-diamine, which we used.[27]

EXPERIMENTAL

The general preparative and spectroscopic techniques were the same as those described in other recent papers from this laboratory.[28]

Di-μ-(NNN′N′-*tetramethylpentane*-1,5-*diamine*-NN′)-*bis*[*dichloropalladium*(II)] *with and without Benzene of Solvation*.—The diamine (0.234 g, 1.48 mmol) was added to a solution of bis(benzonitrile)dichloropalladium(II) (0.516 g, 1.35 mmol) in dichloromethane (10 cm^3). Benzene (*ca.* 2 cm^3) was added and the solution set aside at 20 °C. The precipitate was recrystallized from dichloromethane–benzene to give the required benzene solvated product $[Pd_2Cl_4\{Me_2N(CH_2)_5NMe_2\}_2]\cdot C_6H_6$ as orange *prisms* (0.312 g, 0.417 mmol, 62%). When heated at 100 °C (0.01 mmHg) for 2 h the benzene was lost and the crystals turned light brown, m.p. 150—154 °C (decomp.) [Found: C, 32.2; H, 6.45; Cl, 21.5; N, 8.1%; M (in $CHCl_3$) 659. $C_{18}H_{44}Cl_4N_4Pd_2$ requires C, 32.2; H, 6.6; Cl, 21.1; N, 8.35%; M, 671].

Di-μ-(NNN′N′-*tetramethylheptane*-1,7-*diamine*-NN′)-*bis*[*dichloropalladium*(II)]-*Benzene* (1/1).—This was prepared in a similar manner as yellow needles in 85% yield. When heated at 100 °C (0.01 mmHg) the benzene was lost and the unsolvated binuclear *complex* was obtained, m.p. 126—130 °C (decomp.) [Found: C, 36.5; H, 7.1; Cl, 19.7; N, 7.55%; M (in $CHCl_3$) 708. $C_{22}H_{52}Cl_4N_4Pd_2$ requires C, 36.35; H, 7.2; Cl, 19.5; N, 7.7%; M 727].

Di-μ-(NNN′N′-*tetramethyldecane*-1,10-*diamine*-NN′)-*bis*[*dichloropalladium*(II)].—A solution of the diamine (0.23 g, 1.0 mmol) in ethanol (2 cm^3) was added to a solution of sodium tetrachloropalladate(II) tetrahydrate (0.37 g, 1.0 mmol) in ethanol (10 cm^3). The yellow-brown precipitate which formed was washed with water, dried, and recrystallized from dichloromethane–methanol as yellow microcrystals, 0.17 g (0.41 mmol, 41%) (Found: C, 41.5; H, 8.0; Cl, 17.5%; M 832. $C_{28}H_{64}Cl_4N_4Pd_2$ requires C, 41.2; H, 8.0; Cl, 17.7%; M 812).

NNN′N′-*Tetramethylpentane*-1,5-*diamine*.—A solution of *NNN′N′*-tetramethylglutaramide (8.05 g, 43 mmol) in diethyl ether (200 cm^3) was slowly added to a stirred suspension of $Li[AlH_4]$ (4.5 g, 118 mmol) in ether (100 cm^3). After the addition the mixture was heated under reflux for 8 h, cooled, water (15 cm^3) added, and the product isolated with diethyl ether. The product was a colourless liquid (4.8 g, 30 mmol, 70%), b.p. 85—95 °C (15 mmHg).[*]

NNN′N′-*Tetramethylheptane*-1,7-*diamine*.—A mixture of 1,7-dibromoheptane (4.48 g, 17 mmol) and an ethanol solution of dimethylamine (42.5 cm^3, 33% amine, 105 mmol) was set aside at *ca.* 20 °C for 2 d and then heated under reflux for 4 h. The solvent was removed under reduced pressure, the residue treated with water (25 cm^3) and sodium hydroxide (5 g), and the product isolated with diethyl ether as a colourless liquid, b.p. 110—115 °C (14 mmHg) [lit.,[26] 228—230 °C (760 mmHg)], yield 2.4 g (13 mmol, 74%).

Crystal Data.—$[Pd_2Cl_4\{Me_2N(CH_2)_5NMe_2\}_2]\cdot C_6H_6$, $C_{24}H_{50}Cl_4N_4Pd_2$, $M = 749.3$, Triclinic, $a = 8.425(2)$, $b = 12.624(2)$, $c = 8.217(2)$ Å, $\alpha = 105.16(2)$, $\beta = 98.12(2)$, $\gamma = 71.83(2)^\circ$, $U = 799.8(3)$ Å^3, $D_m = 1.57$ g cm,$^{-3}$ $Z = 1$, $D_c = 1.56$ g cm^{-3}, $F(000) = 382$, space group $P\bar{1}$, Mo-K_α radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 14.67 cm^{-1}. $[Pd_2Cl_4\{Me_2N(CH_2)_7NMe_2\}_2]\cdot C_6H_6$, $C_{28}H_{58}Cl_4N_4Pd_2$, $M = 805.4$, Orthorhombic, $a = 29.387(4)$, $b = 8.030(2)$, $c = 15.177(3)$ Å, $U = 3\ 582(1)$ Å^3, $D_m = 1.49$ g cm^{-3}, $Z = 4$, $D_c = 1.49$ g cm^{-3}, $F(000) = 1\ 656$, space group *Cmca*, μ(Mo-K_α) = 13.15 cm^{-1}.

Structure determinations. Measurements were made on a Syntex $P2_1$ diffractometer using monochromatized radiation, scintillation counting, and pulse-height discrimination. Cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles of 15 reflections with $35 < 2\theta < 40^\circ$. Intensities of all the independent reflections with $5 < 2\theta < 50^\circ$ were measured in the θ—2θ scan mode, with scans running from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$, and scan speeds varying from 2.02 to 29.30° min^{-1}. The structure analyses used the 2 577 intensities having $I > 3\sigma(I)$ for the $Me_2N[CH_2]_5NMe_2$ complex [$254 < 3\sigma(I)$] and the 1 154 with $I > 3\sigma(I)$ for the $Me_2N[CH_2]_7NMe_2$ complex [$472 < 3\sigma(I)$]. These intensities were reduced to F_o by correction for Lorentz, polarization, and transmission factors [$A^* = 1.22$—1.28 and 1.22—1.34 respectively]. The structures were solved from Patterson and electron-density syntheses and refined by least squares. Refinement of co-ordinates and anisotropic temperature factors gave a final R of 0.034 for the $Me_2N[CH_2]_5NMe_2$ complex and 0.057 for the $Me_2N[CH_2]_7NMe_2$ complex with $R' = 0.052$ and 0.070 respectively; hydrogen atoms were not included. Weights were derived from counting statistics, and atomic scattering factors were calculated using the analytical approximation and coefficients in ref. 29. The final atomic co-ordinates and their estimated standard deviations are given in Table 1. Observed and calculated structure-factor amplitudes and anisotropic thermal parameters (as U_{ij} in units of Å^2) are listed in Supplementary Publication No. SUP 22405 (26 pp).[†]

We thank the S.R.C. for support.

[8/886 *Received*, 12*th May*, 1978]

REFERENCES

[1] T. D. O'Brian, in ' Chemistry of the Co-ordination Compounds,' ed. J. Bailar, Reinhold, New York, 1956.

[2] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, p. 652.

[3] A. E. Martell, *Adv. Chem. Ser.*, 1967, **61**, 272.

[4] G. Anderegg, in ' Coordination Chemistry,' ed. A. E. Martell, A.C.S. Monograph, 1971, p. 470.

[5] G. Schwarzenbach, *Helv. Chim. Acta*, 1952, **35**, 2344.

[6] F. A. Cotton and F. E. Harris, *J. Phys. Chem.*, 1955, **59**, 1203.

[7] R. W. Parry, in ' Chemistry of the Coordination Compounds,' ed. J. C. Bailar, Reinhold, New York, 1956, p. 250.

[8] A. J. Pryde, B. L. Shaw, and B. Weeks, *J.C.S. Chem. Comm.*, 1973, 947.

[9] A. J. Pryde, B. L. Shaw, and B. Weeks, *J.C.S. Dalton*, 1976, 322.

[10] F. C. March, R. Mason, K. M. Thomas, and B. L. Shaw, *J.C.S. Chem. Comm.*, 1975, 584.

[11] W. Levason, C. A. McAuliffe, and S. G. Murray, *J. Organometallic Chem.*, 1976, **110**, C25.

[12] W. Levason, C. A. McAuliffe, and S. G. Murray, *J. Organometallic Chem.*, 1975, **101**, C29.

[13] J. C. Chottard, E. Mulliez, J. P. Girault, and D. Munsey, *J.C.S. Chem. Comm.*, 1974, 780.

[14] N. W. Alcock, J. M. Brown, and J. C. Jeffrey, *J.C.S. Dalton*, 1976, 583 and refs. therein.

[15] H. Ogino and J. Fujita, *Bull. Chem. Soc. Japan*, 1975, **48**, 1836.

[16] A. R. Sanger, *J.C.S. Dalton*, 1977, 1971.

[17] B. L. Shaw and I. Shepherd, unpublished work.

[18] H. D. Empsall, R. Markham, B. L. Shaw, and B. Weeks, unpublished work.

[19] B. L. Shaw, *J. Amer. Chem. Soc.*, 1975, **97**, 3856.

[20] F. S. Dainton and K. J. Ivin, *Quart. Rev.*, 1958, **12**, 61.

[21] J. Dale, *Acta Chem. Scand.*, 1973, **27**, 1149.

---

[*] Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[†] For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

[22] F. A. L. Anet and R. Anet, in ' Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, 1975, p. 562.

[23] L. Tschugaeff, *Chem. Ber.*, 1906, **39**, 3190.

[24] A. Werner, *Chem. Ber.*, 1907, **40**, 61.

[25] M. P. A. Meerburg, *Rec. Trav. chim.*, 1899, **18**, 374.

[26] H. T. Clarke, *J. Chem. Soc.*, 1913, 1689.

[27] R. B. Barlow, T. D. M. Roberts, and D. A. Reid, *J. Pharm. Pharmacol.*, 1953, **5**, 35.

[28] H. D. Empsall, E. M. Hyde, and B. L. Shaw, *J.C.S. Dalton*, 1975, 1690.

[29] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol 4.