# Preparation and Crystal Structure of the Sixteen-atom Ring Complex Di-μ-[glutaraldehyde bis(dimethylhydrazone)]-bis[dichloropalladium(II)] †

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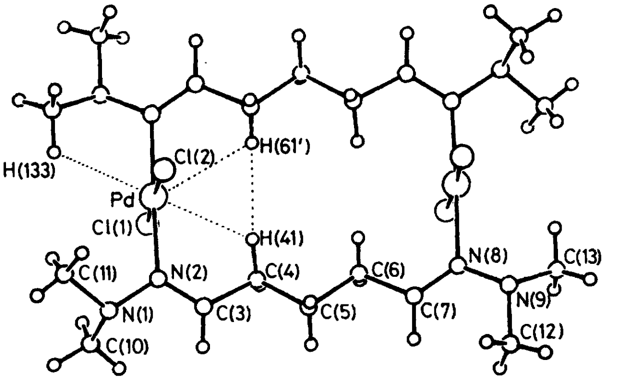
Treatment of [$PdCl_2(NCPh)_2$] with glutaraldehyde bis(dimethylhydrazone) gives the stable 16-atom ring binuclear complex [$Pd_2Cl_4\{Me_2NN=CH(CH_2)_3CH=NNMe_2\}_2$] in high yield. The crystal structure has been determined. The crystals are Triclinic, with unit-cell dimensions $a$ = 8.660(2), $b$ = 11.909(3), $c$ = 7.407(2) Å, $\alpha$ = 106.20(2), $\beta$ = 102.75(2), $\gamma$ = 82.83(2)°, $Z$ = 1, and space group $P\bar{1}$. Factors affecting the conformation and stability of the complex are discussed and the structure is compared with those of other complexes containing large chelate rings.

COMPLEXES containing large chelate rings are relatively rare although several examples have been described recently.[1,2] We have prepared and determined the crystal structures of some binuclear complexes of palladium dichloride of the types [$Pd_2Cl_4(L-L)_2$] {L-L = $Bu^t_2P[CH_2]_nPBu^t_2$ ($n$ = 5, 7,[3] or 10[4]) or $Me_2N[CH_2]_nNMe_2$ ($n$ = 5 or 7)[1]}. These complexes are more thermodynamically stable than their open-chain analogues (precursors) and we have explained this in terms of conformational and entropy effects. If the preferred conformations of an open-chain precursor are similar to those adopted in the large chelate ring then ring formation will not introduce any significant amount of additional strain. An important factor was considered to be the effect of substituents at the ' corner ' positions of the ring.[1,3] Bulky substituents, suitably positioned, would also promote ring formation through entropy effects since their presence would reduce the loss of rotational entropy on cyclisation.[1,3]

We believe that the above factors which influence the relative stabilities of open-chain and large-ring chelate complexes should be generally applicable. Therefore one can make predictions as to what types of ligand are most likely to form stable large-ring chelates. On this basis we predicted that glutaraldehyde bis(dimethylhydrazone) in its ($E$,$E$) form should readily form a stable binuclear chelate [$Pd_2Cl_4\{Me_2NN=CH(CH_2)_3CH=NNMe_2\}_2$] with a sixteen-atom ring. This prediction was based on the following. The bulky $NMe_2$ groups could occupy ' corner ' positions and the two $N=CH-[CH_2]_3CH=N$ chains adopt essentially strain free zigzag conformations with 180° torsion angles. The presence of the four bulky $NMe_2$ groups and four double bonds would mean that the loss of internal rotational entropy which occurs on cyclisation would be relatively small. It has also been shown that when hydrazones such as acetone dimethylhydrazone are complexed to palladium dichloride, *e.g.* in complexes of the type *trans*-[$PdCl_2(Me_2C=NNMeR)_2$] (R = Ph or Me), then the Cl-Pd-Cl chain is held vertical to the $\gt C=NN\lt$ moieties and there is a considerable energy barrier to rotation around the Pd-N bond, leading to the presence of two isomers (rotamers) in solution ($^1H$ n.m.r. evidence).[5,6] We considered that such energy barriers would also confer stability on our proposed large-ring complex [$Pd_2Cl_4\{Me_2NN=CH(CH_2)_3CH=NNMe_2\}_2$] since: (*i*) the Cl-Pd-Cl groups would restrict the number of preferred orientations of the hydrazone groupings in open-chain structures and one of these orientations would be closely similar to that required for cyclisation; and (*ii*) restricted rotation around the Pd-N bonds caused by the chlorine atoms would reduce the loss of internal rotational entropy on cyclisation.

## RESULTS AND DISCUSSION

Treatment of bis(benzonitrile)dichloropalladium(II) with glutaraldehyde bis(dimethylhydrazone)[7] gave the binuclear species [$Pd_2Cl_4\{Me_2NN=CH(CH_2)_3-CH=NNMe_2\}_2$] as orange needles. The yield of recrystallised material was 71% and no other palladium-containing product was detected, *i.e.* the complex appeared to be stable both in the solid state and in solution. Microanalytical, molecular-weight, and characterizing $^1H$ n.m.r. data are given in the Experimental section.



Molecular structure of [$Pd_2Cl_4\{Me_2NN=CH(CH_2)_3CH=NNMe_2\}_2$]. There is a crystallographic centre of symmetry at the molecular centre and the short transannular contacts in one half of the molecule are shown by dotted lines

The molecular structure was determined by $X$-ray diffraction and is shown in the Figure. Bond lengths and angles are given in Table 1 and are normal. Atomic co-ordinates are in Table 2.

The gross features are as we expected, *i.e.* the Cl-Pd-Cl groupings are at right angles to the ' plane ' of the 16-atom ring with the bulky $NMe_2$ groups at the corner positions and the $=CH[CH_2]_3CH=$ groups in the extended

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† No reprints available.

TABLE 1

Bond lengths (Å) and angles (°)

(*a*) Lengths

| | | | |
|---|---|---|---|
| Pd–N(2) | 2.035(3) | Pd–N(8) | 2.057(3) |
| Pd–Cl(1) | 2.294(1) | Pd–Cl(2) | 2.306(1) |
| N(1)–N(2) | 1.435(3) | N(8)–N(9) | 1.400(3) |
| N(2)–C(3) | 1.274(4) | C(7)–N(8) | 1.274(4) |
| C(3)–C(4) | 1.488(4) | C(6)–C(7) | 1.494(5) |
| C(4)–C(5) | 1.518(5) | C(5)–C(6) | 1.507(4) |
| N(1)–C(10) | 1.453(5) | N(9)–C(12) | 1.446(5) |
| N(1)–C(11) | 1.444(5) | N(9)–C(13) | 1.462(4) |
| C(3)–H(3) | 0.98 | C(7)–H(7) | 1.06 |
| C(4)–H(41) | 1.05 | C(6)–H(61) | 0.89 |
| C(4)–H(42) | 1.04 | C(6)–H(62) | 1.10 |
| C(5)–H(51) | 1.01 | C(6)–H(52) | 1.09 |
| C(10)–H(101) | 0.92 | C(12)–H(121) | 0.96 |
| C(10)–H(102) | 0.93 | C(12)–H(122) | 0.89 |
| C(10)–H(103) | 1.03 | C(12)–H(123) | 0.98 |
| C(11)–H(111) | 0.83 | C(13)–H(131) | 1.04 |
| C(11)–H(112) | 0.85 | C(13)–H(132) | 0.94 |
| C(11)–H(113) | 1.02 | C(13)–H(133) | 1.02 |

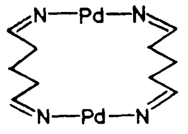
C–H (av.) 0.98, $\sigma = 0.08$

(*b*) Angles

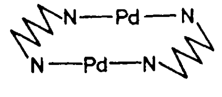
| | | | |
|---|---|---|---|
| N(2)–Pd–Cl(1) | 88.9(1) | N(2)–Pd–Cl(2) | 90.7(1) |
| N(8′)–Pd–Cl(1) | 89.1(1) | N(8′)–Pd–Cl(2) | 91.3(1) |
| N(2)–Pd–N(8′) | 177.3(1) | Cl(1)–Pd–Cl(2) | 177.4(1) |
| Pd–N(2)–C(3) | 121.8(2) | Pd′–N(8)–C(7) | 121.8(2) |
| Pd–N(2)–N(1) | 122.7(1) | Pd′–N(8)–N(9) | 116.5(1) |
| C(3)–N(2)–N(1) | 115.3(2) | C(7)–N(8)–N(9) | 121.1(2) |
| N(2)–C(3)–C(4) | 121.9(3) | C(7)–C(7)–N(8) | 121.1(3) |
| C(3)–C(4)–C(5) | 113.9(2) | C(5)–C(6)–C(7) | 114.9(3) |
| C(4)–C(5)–C(6) | 109.2(2) | | |
| N(2)–N(1)–C(10) | 109.8(2) | N(8)–N(9)–C(12) | 116.3(2) |
| N(2)–N(1)–C(11) | 110.7(2) | N(8)–N(9)–C(13) | 110.8(2) |
| C(10)–N(1)–C(11) | 112.8(2) | C(12)–N(9)–C(13) | 112.7(2) |

Primed atoms are related to the corresponding unprimed atoms by a centre of symmetry at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$).

conformation. The centrosymmetric 16-membered binuclear ring (I) may be compared with that which we found earlier for $[Pd_2Cl_4\{Me_2N(CH_2)_5NMe_2\}_2]$ [1] where the ring system has an elongated chair or 'sofa' con-



(I)



(II)

formation (II). The ring in the present complex is more nearly planar because of the four double bonds, but the departures from planarity are of interest because they lead to short H · · · H and Pd · · · H transannular interactions. The two $-[CH_2]_3-$ chains are turned towards a sofa conformation so that H(41), H(51), and H(61) take up equatorial positions and H(42), H(52), and H(62) become axial. As a result there are three centrosymmetrically related pairs of transannular contacts, with H(41) · · · H(61′) 2.4, H(41) · · · Pd 2.6, and H(61′) · · · Pd 2.7 Å; these are indicated by dotted lines in the Figure.[*] All these short contacts would be avoided if the ring atoms were more nearly coplanar, suggesting that these interactions are attractive in nature. Furthermore, a hydrogen atom of one of the $NMe_2$ groups takes up a position 2.6 Å from Pd. Again this contact is avoidable (as it is avoided by the other $NMe_2$ group) suggesting the existence of an attractive Pd · · · H interaction near the axial position of Pd.

Although the hydrogen atoms were not located in the crystal-structure determination of $[PdCl_2\{Me_2C{=}NNMePh\}_2]$,[8] Pd · · · H distances (for MeC=N hydrogen) were estimated to be very short (2.36 Å).[5] The structural determination was not particularly accurate, however, owing to twinning of the crystal. Pd · · · H distances for hydrogen of methyl bonded to nitrogen were not calculated, but from the published projections these also appear to be short and within an interactive distance. Such interactions may not significantly influence the relative stabilities of our large-ring chelate and an open-chain isomer since they could occur in both.

TABLE 2

Atomic co-ordinates with estimated standard deviations in parentheses

| Atom | *X* | *Y* | *Z* |
|---|---|---|---|
| Pd(1) | 0.238 5(1) | 0.754 0(1) | 0.656 8(1) |
| Cl(1) | 0.060 4(1) | 0.720 4(1) | 0.371 0(1) |
| Cl(2) | 0.425 4(1) | 0.781 3(1) | 0.937 6(1) |
| N(1) | 0.330 3(3) | 0.975 3(2) | 0.585 0(4) |
| N(2) | 0.359 0(2) | 0.850 7(2) | 0.553 8(3) |
| C(3) | 0.455 9(3) | 0.802 9(2) | 0.443 2(5) |
| C(4) | 0.488 5(4) | 0.673 6(2) | 0.383 9(5) |
| C(5) | 0.652 6(3) | 0.635 7(2) | 0.338 3(5) |
| C(6) | 0.677 1(4) | 0.504 0(3) | 0.296 4(6) |
| C(7) | 0.834 4(4) | 0.454 2(2) | 0.247 6(5) |
| N(8) | 0.884 5(2) | 0.349 5(2) | 0.251 5(3) |
| N(9) | 1.036 4(3) | 0.305 4(2) | 0.219 1(4) |
| C(10) | 0.226 2(5) | 1.002 1(3) | 0.417 4(6) |
| C(11) | 0.269 6(4) | 1.025 9(3) | 0.758 9(6) |
| C(12) | 1.121 8(4) | 0.378 0(3) | 0.153 0(5) |
| C(13) | 1.033 6(4) | 0.184 4(3) | 0.101 1(6) |
| H(31) | 0.490 2 | 0.848 0 | 0.369 4 |
| H(41) | 0.482 9 | 0.650 9 | 0.509 8 |
| H(42) | 0.408 6 | 0.640 6 | 0.257 4 |
| H(51) | 0.648 7 | 0.656 8 | 0.215 0 |
| H(52) | 0.745 1 | 0.664 1 | 0.463 7 |
| H(61) | 0.665 4 | 0.475 6 | 0.391 5 |
| H(62) | 0.589 4 | 0.474 5 | 0.164 7 |
| H(71) | 0.890 1 | 0.507 6 | 0.191 0 |
| H(101) | 0.130 1 | 0.969 8 | 0.386 2 |
| H(102) | 0.274 0 | 0.972 2 | 0.311 0 |
| H(103) | 0.203 5 | 1.091 3 | 0.448 8 |
| H(111) | 0.249 3 | 1.096 9 | 0.764 9 |
| H(112) | 0.174 3 | 1.006 7 | 0.729 3 |
| H(113) | 0.348 9 | 1.001 5 | 0.867 8 |
| H(121) | 1.061 6 | 0.397 9 | 0.039 2 |
| H(122) | 1.208 5 | 0.337 0 | 0.118 6 |
| H(123) | 1.148 9 | 0.441 4 | 0.268 8 |
| H(131) | 0.965 9 | 0.177 8 | −0.035 3 |
| H(132) | 1.139 1 | 0.154 2 | 0.095 8 |
| H(133) | 0.983 4 | 0.136 1 | 0.164 3 |

## EXPERIMENTAL

The general preparative techniques and instruments were the same as those used previously.[9]

*Di-μ-[glutaraldehyde bis(dimethylhydrazone)]-bis[dichloropalladium*(II)*]*, $[Pd_2Cl_4\{Me_2NN{=}CH(CH_2)_3CH{=}NNMe_2\}_2]$.—

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[*] The hydrogen positions are taken directly from a difference map without least-squares adjustment of their co-ordinates, but the scatter of the twenty C–H bond lengths indicates that they have a positional standard deviation of 0.08 Å together with the usual systematic shortening of *ca.* 0.1 Å.

Glutaraldehyde bis(dimethylhydrazone) (0.134 g, 0.73 mmol) was added to a solution of bis(benzonitrile)dichloropalladium(II) (0.26 g, 0.68 mmol) in dichloromethane (5 $cm^3$). A precipitate formed rapidly but then dissolved to give a yellow solution. This was set aside for 1.5 h, the solvent was then removed under reduced pressure, and the residue recrystallised from dichloromethane–methanol. This gave the required product as orange needles (0.175 g, 0.24 mmol, 71%), m.p. 129—133 °C (decomp.) [Found: C, 29.85; H, 5.4; Cl, 19.35; N, 15.25%; $M$ (in $CHCl_3$) 733. $C_{18}H_{40}Cl_4N_8Pd_2$ requires C, 19.9; H, 5.55; Cl, 19.6; N, 15.5%; $M$ 723]. Hydrogen-1 n.m.r. data in $CDCl_3$: $\delta$ 3.1 (s) ($NMe_2$), 7.2 (t) [$^3J$(H–H) 6 Hz, N=CH], 3.5—4.1 (br m) ($CH_2CH_2CH_2$), 1.7—2.4 (br m) ($CH_2CH_2CH_2$).

*Crystal Data.*—$C_{18}H_{40}Cl_4N_8Pd_2$, $M = 723.2$, Triclinic, $a = 8.660(2)$, $b = 11.909(3)$, $c = 7.407(2)$ Å, $\alpha = 106.20(2)$, $\beta = 102.75(2)$, $\gamma = 82.83(2)^\circ$, $U = 713.8(3)$ Å$^3$, $Z = 1$, $D_c = 1.682$ g $cm^{-3}$, $F(000) = 364$, space group $P\bar{1}$, graphite-monochromatised Mo-$K_\alpha$ radiation, $\lambda = 0.710\,69$ Å, $\mu$(Mo-$K_\alpha$) = 16.44 $cm^{-1}$.

*Structure Determination.*—Measurements were made on a Syntex $P2_1$ diffractometer, and the crystal used was a needle of dimensions 0.05 × 0.15 × 1.2 mm. Cell dimensions and their standard deviations were determined by least-squares treatment of the setting angles of 15 reflections having $35 < 2\theta < 40^\circ$. Intensities of all independent reflections with $5 < 2\theta < 50^\circ$ were measured in the $\theta$—$2\theta$ scan mode, with scans from 0.8° below $K_{\alpha_1}$ to 0.8° above $K_{\alpha_2}$. The structure analysis used the 2 371 reflections having $I > 3\sigma(I)$, where $\sigma(I)$ was calculated from counting statistics; another 156 reflections below this threshold were excluded as ' unobserved '. The intensities were corrected for Lorentz, polarisation, and transmission ($A^* = 1.17$—$4.75$) factors, and used for solution of the structure by Patterson and electron-density syntheses. Least-squares refinement of the co-ordinates and anisotropic vibration parameters of non-hydrogen atoms converged at $R = 0.040$. A difference-map then showed the 20 hydrogen atoms as peaks of height 0.42—0.65 eÅ$^{-3}$, with four higher peaks of 0.8—1.0 eÅ$^{-3}$ close to the palladium position. The hydrogens were included as fixed contributions with $U_{iso.} = 0.05$ Å$^2$ and further refinement converged at $R = 0.032$, $R' = 0.046$. In the final stages of the refinement the weights based on counting statistics were modified by inclusion of an empirical term $\sigma(I)^2 = \sigma_c(I)^2 + (QI)^2$, where $w^{-1} = \sigma(F)^2 = \sigma_c(F)^2 + 0.25(QF)^2$. A value of $Q = 0.04$ was found to give a uniform distribution of $\langle w\Delta^2\rangle$ as a function of $F_o$. The final value of $[\Sigma w\Delta^2/(n - m)]^{\frac{1}{2}} = 1.92$. Atomic scattering factors were calculated using the analytical approximation and coefficients given in ref. 10, those for hydrogen being the spherically bonded values of Stewart *et al.*[11] The atomic co-ordinates and their estimated standard deviations (by inversion of the 9 × 9 block-diagonal least-squares matrix) are given in Table 2. Vibrational parameters and observed and calculated structure factors are listed in Supplementary Publication No. SUP 22468 (17 pp.).*

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

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