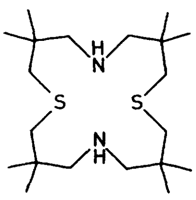
# Stereochemistry of Metal Complexes of the Macrocycle 3,3,7,7,11,11,15,15-Octamethyl-1,9-dithia-5,13-diazacyclohexadecane. Crystal Structure Analysis of 3,3,7,7,11,11,15,15-Octamethyl-1,9-dithia-5,13-diazacyclohexadecanepalladium(II) Dichloride Dihydrate †

**George Ferguson,* Robert McCrindle,* Alan J. McAlees, Masood Parvez, and (in part) Donald K. Stephenson**
*Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1*

Crystals of the title compound are monoclinic, space group *Pn*, with $a$ = 10.533(3), $b$ = 14.994(5), $c$ = 17.214(4) Å, $\beta$ = 96.58(2)°, and $Z$ = 4. In the asymmetric unit there are two independent $[PdL]^{2+}$ cations separated by, and hydrogen-bonded to, two independent chains of hydrogen-bonded water and chloride ions. The cations have different configurations, *c,c,c* and *c,c,t*(N); the Pd atoms have distorted square-planar geometry [Pd–S 2.290(5)—2.297(6) and Pd–N 2.05(2)—2.14(2) Å] with one $Cl^-$ ion in each case in a distant axial position (Pd · : · Cl 3.20 and 3.68 Å). The solid-state structures allow us to rationalize the effect of trace amounts of water on the isomer population of the title compound when dissolved in non-polar solvents, in which the two major species present also have the ligand in the *c,c,c* and *c,c,t*(N) configurations.

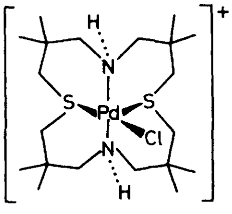
We have described [1] the preparation of 1 : 1 complexes of palladium(II) chloride and palladium(II) hexafluorophosphate with the title macrocycle (L). While solutions of the complexes of both appeared ($^1$H n.m.r.) to consist of isomeric mixtures, crystallization of the hexafluorophosphate gave a single isomer. An *X*-ray structural determination of this showed [1] it to contain square-planar $Pd^{2+}$ cations with the ligand in the *c,t,c* configuration (see Figure 1). Attempts to crystallize the chloride gave material which, upon drying, crumbled and analyzed for $C_{20}H_{42}Cl_2N_2PdS_2{\cdot}H_2O$ (1). $^1$H N.m.r. spectra of this product varied with solvent and were rationalized by postulating that in water, square-planar $Pd^{2+}$ species are present, while in less polar solvents, the two major species which are observed contain five-co-ordinate palladium. In these two species, the four ligand heteroatoms and one chloride define a trigonal bipyramid with the ligand having in one case (2) the *c,c,c* and, in the other (3), the *c,c,t*(N) configuration (see Figure 1). By recrystallization of (1) from acetonitrile–toluene we have now obtained crystals of a dihydrate (4) which proved suitable for *X*-ray structural studies.



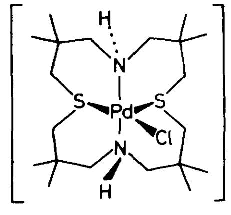
L

## Experimental

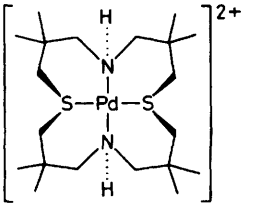
A sample [1] of (1) was recrystallized from moist acetonitrile–toluene (*ca.* 9 : 1) to give a better than 90% recovery of crystalline material which proved to be $[PdL]Cl_2{\cdot}2H_2O$ (4).



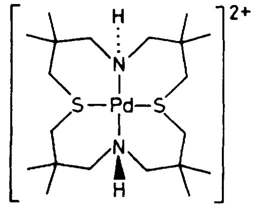
(2)



(3)



(4a)



(4b)

*Crystal Data for* $[PdL]Cl_2{\cdot}2H_2O$ (4).—$C_{20}H_{42}Cl_2N_2PdS_2{\cdot}2H_2O$, $M$ = 588.0, $a$ = 10.533(3), $b$ = 14.994(5), $c$ = 17.214(4) Å, $\beta$ = 96.58(2)°, $U$ = 2 701.2 Å$^3$, $Z$ = 4, $D_c$ = 1.44 g cm$^{-3}$, $F(000)$ = 1 232, Mo-$K_\alpha$ radiation, $\lambda$ = 0.710 69 Å, $\mu$(Mo-$K_\alpha$) = 10.35 cm$^{-1}$. Space group *Pn* ($C_s^2$, no. 7) or *P*2/*n* ($C_{2h}^4$, no. 13) from systematic absences ($h0l$ absent if $h + l = 2n + 1$); *Pn* chosen, and confirmed by the analysis.

A crystal measuring 0.30 × 0.12 × 0.10 mm was used for data collection with an Enraf–Nonius CAD4 diffractometer. Following preliminary photographic studies, accurate unit-cell data and the crystal-orientation matrix were determined from a least-squares refinement of the setting angles of 25 reflections with $10 \leqslant \theta \leqslant 15°$. Intensity data were collected in the range $2 \leqslant \theta \leqslant 20°$ by the $\omega/2\theta$ scan method using monochromatic Mo-$K_\alpha$ radiation. The intensities of three reflections, chosen as standards, were monitored every hour of exposure time and showed no significant variation. Intensities of 2 822 unique reflections were measured of which 2 462 had $I \geqslant 3\sigma(I)$ and were used in the structure solution and refinement. Data were corrected for Lorentz and polarization factors and for absorption. Maximum and minimum values of the transmission coefficients are 0.9047 and 0.8774 respectively.

---

† *Supplementary data available* (No. SUP 23639, 21 pp.): structure factors, thermal parameters, full list of bond lengths, bond angles, torsion angles, and intermolecular contacts, stereoviews of cations (*a*) and (*b*) and unit-cell contents. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

**Table 1.** Final fractional co-ordinates (× $10^4$) with estimated standard deviations in parentheses for $[PdL]Cl_2 \cdot 2H_2O$ (4)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pd(1) | 0 | 1 159(1) | 0 |
| Pd(2) | 5 097(1) | 6 267(1) | 458(1) |
| S(1) | 605(6) | 1 679(3) | 1 242(3) |
| S(2) | −491(5) | 725(3) | −1 274(3) |
| S(3) | 4 539(6) | 6 762(3) | −795(3) |
| S(4) | 5 571(5) | 5 776(3) | 1 722(3) |
| Cl(1) | 177(6) | −1 143(4) | 864(4) |
| Cl(2) | −4 683(6) | −1 149(3) | 1 147(4) |
| Cl(3) | 748(19) | 3 411(11) | −662(6) |
| Cl(4) | 5 645(15) | 4 489(11) | −479(8) |
| O(1) | 2 676(19) | −2 226(12) | 1 189(11) |
| O(2) | −2 064(17) | 107(11) | 1 158(9) |
| O(3) | 3 783(43) | 2 831(28) | −481(23) |
| O(4) | 8 361(54) | 4 969(39) | −836(30) |
| N(1) | 1 689(15) | 364(9) | 40(8) |
| N(2) | −1 812(19) | 1 689(12) | 27(11) |
| N(3) | 3 478(19) | 5 504(12) | 311(10) |
| N(4) | 6 797(15) | 7 034(9) | 563(8) |
| C(1) | 2 268(21) | 1 951(12) | 1 211(12) |
| C(2) | 3 132(22) | 1 188(11) | 1 119(12) |
| C(3) | 2 953(20) | 762(12) | 321(11) |
| C(4) | 3 011(23) | 488(15) | 1 740(13) |
| C(5) | 4 485(25) | 1 547(15) | 1 201(14) |
| C(6) | 1 750(18) | −295(11) | −573(10) |
| C(7) | 1 895(21) | 60(13) | −1 382(12) |
| C(8) | 1 029(20) | 851(13) | −1 639(11) |
| C(9) | 3 280(27) | 286(15) | −1 488(15) |
| C(10) | 1 472(24) | −707(15) | −1 979(14) |
| C(11) | −1 257(23) | 1 731(12) | −1 681(12) |
| C(12) | −2 676(24) | 1 753(14) | −1 470(13) |
| C(13) | −2 714(22) | 1 438(14) | −569(13) |
| C(14) | −3 491(27) | 1 075(14) | −1 989(15) |
| C(15) | −3 156(27) | 2 695(16) | −1 671(14) |
| C(16) | −2 027(23) | 2 570(16) | 282(13) |
| C(17) | −1 396(18) | 2 864(11) | 1 147(10) |
| C(18) | −46(19) | 2 826(16) | 1 215(17) |
| C(19) | −1 829(30) | 3 836(16) | 1 138(17) |
| C(20) | −2 188(37) | 2 413(24) | 1 710(21) |
| C(21) | 2 911(24) | 7 099(14) | −794(14) |
| C(22) | 2 026(24) | 6 285(12) | −769(13) |
| C(23) | 2 201(49) | 6 015(25) | 147(27) |
| C(24) | 2 169(33) | 5 692(21) | −1 427(18) |
| C(25) | 540(41) | 6 727(24) | −719(22) |
| C(26) | 3 347(27) | 4 776(17) | 904(14) |
| C(27) | 3 190(22) | 5 066(13) | 1 773(12) |
| C(28) | 4 013(21) | 5 854(13) | 2 059(12) |
| C(29) | 1 789(32) | 5 344(19) | 1 916(18) |
| C(30) | 3 596(26) | 4 233(17) | 2 256(15) |
| C(31) | 6 400(23) | 6 702(13) | 2 174(12) |
| C(32) | 7 773(20) | 6 798(11) | 1 969(11) |
| C(33) | 7 888(22) | 6 618(13) | 1 138(12) |
| C(34) | 8 616(24) | 6 094(12) | 2 455(13) |
| C(35) | 8 273(27) | 7 712(16) | 2 188(14) |
| C(36) | 7 379(19) | 7 121(12) | −228(10) |
| C(37) | 6 773(21) | 7 798(14) | −792(12) |
| C(38) | 5 269(24) | 7 855(14) | −798(13) |
| C(39) | 7 288(28) | 8 732(15) | −614(15) |
| C(40) | 7 026(24) | 7 573(15) | −1 603(13) |

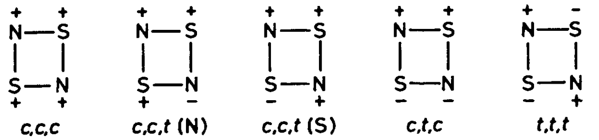


**Figure 1.** The five possible configurations of L when acting as a quadridentate ligand; the positive and negative signs denote the relative orientations of the NH protons and the S lone pairs with respect to the ring plane

The structure was solved by the heavy-atom method. There are two independent cations, four $Cl^-$ ions, and four water molecules in the asymmetric unit. Initial refinement using the SHELX system of programs[2] by full-matrix least-squares calculations with isotropic thermal parameters lowered $R$ to 0.132; this was followed by six cycles of full-matrix refinement with anisotropic thermal parameters for the Pd, S, and Cl atoms and isotropic vibration parameters for the N, C, and O atoms. The hydrogen atoms were not included in the refinement. In the final cycles of refinement a weighting scheme of the form $w = 1/[\sigma^2 F + pF^2]$ was employed where the final $p$ parameter refined to 0.0112. Scattering factors used in the calculations were taken from ref. 3, and allowance was made for anomalous dispersion.[4] Refinement converged with $R = 0.074$ and $R' = [\Sigma w\Delta^2/\Sigma wF_o{}^2]^{\frac{1}{2}} = 0.079$. A final difference map showed a few maxima (0.5—1.0 e $Å^{-3}$) in positions expected for hydrogen, and was devoid of any other significant features. The final fractional co-ordinates and their standard deviations are shown in Table 1 and details of molecular dimensions are summarized in Table 2. Figure 2 contains views of the two independent cations showing the atom-numbering scheme used.

**Table 2.** Selected molecular dimensions with estimated standard deviations in parentheses for $[PdL]Cl_2 \cdot 2H_2O$ (4)

(*a*) Bond distances (Å)

| | | | |
|---|---|---|---|
| Pd(1)–S(1) | 2.296(5) | Pd(2)–S(3) | 2.293(6) |
| Pd(1)–S(2) | 2.290(5) | Pd(2)–S(4) | 2.297(6) |
| Pd(1)–N(1) | 2.136(15) | Pd(2)–N(3) | 2.045(19) |
| Pd(1)–N(2) | 2.074(20) | Pd(2)–N(4) | 2.119(15) |

Mean values for other bond lengths are: S–C 1.81(2), N–C 1.49(3), C($sp^3$)–C($sp^3$) 1.54(5)

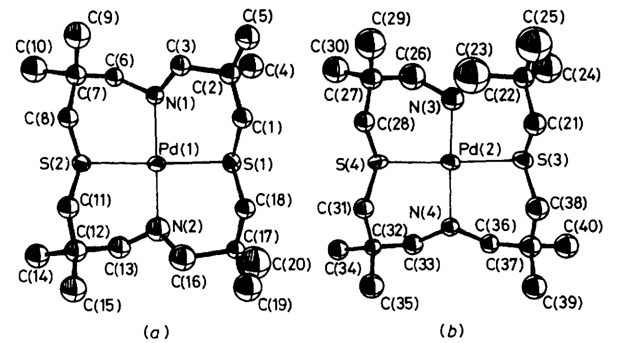
(*b*) Angles (°)

| | | | |
|---|---|---|---|
| S(1)–Pd(1)–S(2) | 175.3(2) | S(3)–Pd(2)–S(4) | 177.7(2) |
| S(1)–Pd(1)–N(1) | 91.1(4) | S(3)–Pd(2)–N(3) | 86.8(5) |
| S(1)–Pd(1)–N(2) | 90.4(5) | S(3)–Pd(2)–N(4) | 91.6(4) |
| S(2)–Pd(1)–N(1) | 88.2(4) | S(4)–Pd(2)–N(3) | 91.5(5) |
| S(2)–Pd(1)–N(2) | 91.3(5) | S(4)–Pd(2)–N(4) | 90.2(4) |
| N(1)–Pd(1)–N(2) | 168.2(7) | N(3)–Pd(2)–N(4) | 177.5(6) |
| Pd(1)–S(1)–C(1) | 102.5(7) | Pd(2)–S(3)–C(21) | 103.5(8) |
| Pd(1)–S(1)–C(18) | 103.3(6) | Pd(2)–S(3)–C(38) | 103.5(8) |
| Pd(1)–S(2)–C(8) | 101.1(6) | Pd(2)–S(4)–C(28) | 100.2(7) |
| Pd(1)–S(2)–C(11) | 100.1(7) | Pd(2)–S(4)–C(31) | 102.0(7) |
| Pd(1)–N(1)–C(3) | 119.9(11) | Pd(2)–N(3)–C(23) | 116.2(18) |
| Pd(1)–N(1)–C(6) | 117.5(11) | Pd(2)–N(3)–C(26) | 117.3(15) |
| Pd(1)–N(2)–C(13) | 116.0(15) | Pd(2)–N(4)–C(33) | 113.0(10) |
| Pd(1)–N(2)–C(16) | 123.0(16) | Pd(2)–N(4)–C(36) | 112.5(10) |

Mean values for other bond angles are: C–S–C 99.8(10), C–N–C 109.8(17), S–C–C 112.0(14), N–C–C 116.5(18), C–C–C 109.3(19).

## Results and Discussion

The asymmetric unit of (4) contains two independent $[PdL]^{2+}$ cations, four $Cl^-$ ions, and four water molecules. The cations have quite different configurations as shown by the ring torsion angles and Figure 2. In cation (*a*), which contains



(*a*) (*b*)

**Figure 2.** Views of the two independent $[PdL]^{2+}$ cations (*a*) and (*b*)

Pd(1) [Figure 2(*a*)], there is approximate mirror symmetry [through S(2)–Pd(1)–S(1)]; two of the rings [Pd(1),S(1), C(1),C(2),C(3),N(1) and Pd(1),S(1),C(18),C(17),C(16),N(2)] have chair conformations, the other two have twisted boat conformations; the N–H groups are required to be *cis*, and the *c,c,c* configuration (Figure 1) is adopted. In cation (*b*), which contains Pd(2) [Figure 2(*b*)], only one ring [Pd(2), S(3),C(21),C(22),C(23),N(3)] is in a chair conformation, the remaining rings have twist-boat conformations; the N–H groups are required to be *trans*, and the configuration adopted is *c,c,t*(N). Studies of molecular models of these two configurations show that they may be simply interconverted. For example, in cation (*a*), inversion of the N(2)–H moiety with a concomitant movement of the C(16) and C(17) atoms yields the *c,c,t*(N) configuration found in cation (*b*).

The Pd atoms have slightly distorted square-planar coordination with dimensions [Pd–S 2.290(5)—2.297(6), mean 2.294(6); Pd–N 2.05(2)–2.14(2), mean 2.09(2) Å; Pd–S–C 100.1(7)—103.5(8); Pd–N–C 113(1)—123(2)°] in accord with those found in the centrosymmetric $[PdL]^{2+}\cdot 2PF_6^-$ structure.[1]

In the crystal structure, chloride ions and water molecules form two different, independent, hydrogen-bonded chains which both extend along the *a* direction and have alternating $H_2O$ molecules and $Cl^-$ ions with O–H · · · Cl 3.08—3.42 Å. These chains are separated by, and hydrogen-bonded to, the two independent cations (*a*) and (*b*), to form sheets in the *xy* plane at $z = 0, \frac{1}{2}$, *etc*. Only van der Waals interactions occur between the sheets. The hydrogen-bonding pattern within a sheet is shown in Figure 3. Cation (*a*), with *cis* N–H groups, is hydrogen-bonded to only one water–chloride chain *via* N(1)–H · · · Cl(1) (3.19 Å) and N(2)–H · · · O(2) (3.10 Å) hydrogen bonds. The shortest contact between cation (*a*) and the other independent water–chloride chain is a Pd(1) · · · Cl(3) contact of 3.68 Å [which places Cl(3) in an axial position relative to the Pd(1) co-ordination plane]. On the other hand, cation (*b*), with *trans* N–H groups, is linked to both water–chloride chains *via* N(3)–H · · · Cl(4) (3.18 Å) and N(4)–H · · · Cl(2) (3.35 Å) hydrogen bonds and also *via* a short Pd(2) · · · Cl(4) contact (3.20 Å) [which places Cl(4) in a pseudo-axial position relative to the Pd(2) coordination plane].

Interestingly, the two ligand configurations found in this crystal, namely *c,c,c* and *c,c,t*(N), are the same as those deduced[1] for solutions. There have been relatively few structural studies on metal complexes of saturated 16-membered ring macrocycles related to the ligand L. *X*-Ray structural studies[5] on a series of molybdenum complexes of 1,5,9,13-tetrathiacyclohexadecane have revealed that the ligand adopts the *c,c,c* configuration with the six-membered chelate rings all in essentially chair conformations. The *c,c,c* geometry is apparently[6] adopted by the ligand in one of the isomers (at least three) found in solutions of *trans*-dichloro-(1,5,9,13-tetra-azacyclohexadecane)nickel(II). It was suggested[6] that the chelate rings in this isomer all have chair conformations. Finally, the ligand in two isomers of *trans*-dichloro(1,5,9,13-tetra-azacyclohexadecane)cobalt(III) perchlorate has been suggested[7] to have the *c,t,c* and *c,c,t* configurations on the basis of models and conformational energy considerations assuming the presence of two chairs and two twist-boats for both. Thus, the ring conformations found in the present study differ from those suggested and found, respectively, for the more symmetrical tetra-aza- and tetrathia-macrocycles.

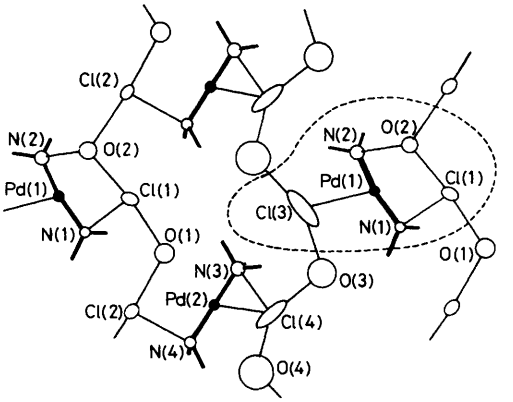


**Figure 3.** View along [001] showing part of the hydrogen-bonded sheet. For clarity only the Pd and N atoms and the bonds from the N atoms are shown for each PdL moiety. Hydrogen bonds are shown by thin lines. A configuration similar to that enclosed in dots may be maintained in solution

In the crystal, one of the two chloride ions associated with each palladium [Cl(3)/Pd(1); Cl(4)/Pd(2)] is clearly in a better position to approach more closely and bond with the metal than is the other. Such a close approach may take place when the solid is dissolved in a relatively non-polar solvent. Concomitant folding of the ligand around the N–Pd–N axis and away from the approaching chloride would produce the trigonal bipyramidal species (with axial nitrogens) suggested[1] to be present in such solutions. The solid-state structure also enables us to rationalize the observation that azeotroping water out of deuteriochloroform solutions of (1) results in an increase in the relative amounts of the complex (3) with the ligand in the *c,c,t*(N) configuration. If the part structure enclosed by dots in Figure 3 is maintained by (2) when the complex is dissolved, but is disrupted when water is azeotroped from the solution, then (3) may become the thermodynamically preferred product, where both chlorides can hydrogen-bond simultaneously.

## Acknowledgements

We are grateful to the Natural Sciences and Engineering Research Council of Canada for Grants in Aid of Research (to G. F. and R. McC.).

## References

1 R. McCrindle, G. Ferguson, A. J. McAlees, M. Parvez, and D. K. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1982, 1291.
2 G. M. Sheldrick, SHELX system of programs for structure determination, Cambridge University, 1976.

3 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321; R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

4 D. T. Cromer and D. L. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

5 R. E. DeSimone, J. Cragel, W. H. Ilsley, and M. D. Glick, *J. Coord. Chem.*, 1979, **9**, 167; R. E. DeSimone and M. D. Glick, *Inorg. Chem.*, 1978, **17**, 3574; J. Cragel, V. B. Pett, M. D. Glick, and R. E. DeSimone, *ibid.* 1978, **17**, 2885.

6 A. Dei, *Inorg. Chim. Acta*, 1981, **53**, L155.

7 Y. Hung, L. Y. Martin, S. C. Jackels, A. M. Tait, and D. H. Busch, *J. Am. Chem. Soc.*, 1977, **99**, 4029.

*Received 29th November* 1982; *Paper* 2/2002