

There are none of the short Au...Au contacts (the shortest is 9.7 Å) that appear to be an indispensable factor in the stability of a number of gold(I) complexes where inter- and intramolecular Au...Au contacts in the range 2.76–3.40 Å have been observed (Hesse & Jennische, 1972; Lawton *et al.*, 1972; Drew & Riedl, 1973; Crane & Beall, 1978; Jones, Sheldrick, Uson & Laguna, 1980).

The geometry observed for the cation, [PPh₄]⁺, is as expected. The P–C bond lengths (mean 1.78 Å) do not differ significantly from literature values (Coucovanis, Stremple, Simhon, Swenson, Baenziger, Draganjac, Chan, Simopoulos, Papaefthymiou, Kostikas & Petrouleas, 1983; Ciani, Manassero & Seroni, 1980); similarly the C–P–C angles, which lie in the range 104.6 (7)–112.9 (7)°, are unexceptional.

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References

- BAENZIGER, N. C., BENNETT, W. E. & SOBOROFF, D. M. (1976). *Acta Cryst.* **B32**, 962–963.
- BECK, W., STETTNER, K. H., TODROS, S. & SCHWARZHAUS, K. E. (1967). *Chem. Ber.* **100**, 3944–3954.
- BLUNDELL, T. L. & POWELL, H. M. (1971). *J. Chem. Soc. A*, pp. 1685–1690.
- BOWMAKER, G. A. & DOBSON, B. C. (1981). *J. Chem. Soc. Dalton Trans.* pp. 267–270.
- CIANI, G., MANASSERO, M. & SERONI, A. (1980). *J. Organomet. Chem.* **199**, 271–279.
- COUCOVANIS, D., STREMPLE, P., SIMHON, D., SWENSON, D., BAENZIGER, N. C., DRAGANJAC, M., CHAN, L. T., SIMOPOULOS, A., PAPAETHYMIU, V., KOSTOKAS, A. & PETROULEAS, V. (1983). *Inorg. Chem.* **22**, 293–308.
- CRANE, W. S. & BEALL, H. (1978). *Inorg. Chim. Acta*, **31**, L469–L470.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DREW, M. G. B. & RIEDL, M. J. (1973). *J. Chem. Soc. Dalton Trans.* pp. 52–55.
- ENRAF–NONIUS (1980). *Structure Determination Package*. Enraf–Nonius, Delft.
- GUY, J. J., JONES, P. G. & SHELDRIK, G. M. (1976). *Acta Cryst.* **B32**, 3321–3322.
- HESSE, R. & JENNISCHE, P. (1972). *Acta Chem. Scand.* **26**, 3855–3864.
- HITCHCOCK, P. B. & PYE, P. L. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1457–1460.
- HUHEEY, J. E. (1975). *Inorganic Chemistry*, pp. 184–185 and references therein. New York: Harper & Row.
- ISAB, A. A. & SADLER, P. J. (1976). *J. Chem. Soc. Chem. Commun.* pp. 1051–1052.
- JONES, P. G., SHELDRIK, G. M., USON, R. & LAGUNA, A. (1980). *Acta Cryst.* **B36**, 1486–1488.
- LAWTON, S. L., ROHRBAUGH, W. J. & KOKOTAILO, G. T. (1972). *Inorg. Chem.* **11**, 2227–2233.
- MAIER, W. (1961). *Angew. Chem.* **73**, 120.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 224. Ithaca, New York: Cornell Univ. Press.
- RUBEN, H., ZALKIN, A., FALTENS, M. O. & TEMPLETON, D. H. (1974). *Inorg. Chem.* **13**, 1836–1839.
- SHELDRIK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
- THOMAS, R., SHOEMAKER, C. B. & ERIKS, K. (1966). *Acta Cryst.* **21**, 12–20.

Acta Cryst. (1985). **C41**, 865–869

The Structure of *cis*-Dichloro(25-ethoxycarbonyl-2,3,7,8,12,13,17,18-octaethyl-23,24-methano-23*H*,24*H*-porphyrin-*N*²¹,*N*²²,*H*)palladium(II) Chloroform Solvate, [PdCl₂(C₄₀H₅₀N₄O₂)]·CHCl₃

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Dedicated to Professor Dorothy Hodgkin on the occasion of her 75th birthday

Abstract. *M_r* = 915.56, orthorhombic, *Pbca*, *a* = 16.577 (4), *b* = 26.325 (6), *c* = 19.951 (5) Å, *U* =

8706.4 Å³, *Z* = 8, *D_m* = 1.38 (by flotation in aqueous KI), *D_x* = 1.397 g cm⁻³, Mo *Kα*, λ = 0.71069 Å, μ = 6.95 cm⁻¹, *F*(000) = 3776.4, *T* = 295 K, *R* = 0.065, *wR* = 0.053 for 2442 observed reflections [*F_o* ≥ 3σ(*F_o*)]. The PdCl₂ and ethyl acetate groups are bonded to the two opposite pairs of *cis*-N pyrrole atoms and not to the same pair as postulated from chemical

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and spectroscopic investigations. The porphyrin macrocycle is very folded, as illustrated by the dihedral angles of the pyrrole rings with the mean plane defined by atoms N(21), N(22), N(23) and N(24): 25.4, 19.3, -14.1 and -16.9° (e.s.d.'s *ca* 0.5°) for N(21) to N(24) pyrrole rings, respectively. Displacements of N atoms from the above plane are 0.026 (10), -0.026 (9), 0.029 (9) and -0.029 (9) Å for N(21) to N(24), respectively. The coordination of the Pd atom is very unusual since it represents a case of rare five coordination for Pd^{II}. It is best described as square-planar with a trigonal-bipyramidal distortion. The fifth coordination site of the Pd atom is occupied by H(37) [Pd...H(37) = 2.47 Å].

Introduction. In connection with considerations of the mechanism of the biochemical rearrangements controlled by cobalamin-containing enzymes, the condensation of ethyl diazoacetate with various cobalt complexes of octaethylporphyrin was studied to check the assumption that a cobalt carbene is an intermediate in the above rearrangements (Batten, Hamilton, Johnson, Shelton & Ward, 1974; Johnson, Ward, Batten, Hamilton, Shelton & Elson, 1975). Various *N,N'*-*cis*-bridged porphyrins and their metal complexes were obtained in the course of this work and were first examples of this type of porphyrin. It seemed interesting to undertake an X-ray study of these compounds to confirm their structures as postulated on the basis of synthetic and mass spectroscopy results. The structure of 25-ethoxycarbonyl-2,3,7,8,12,13,17,18-octaethyl-21,22-methano-21*H*,22*H*-porphyrin hydrobromide has been solved and reported previously (Bartczak, 1985). This investigation fully confirmed the structure proposed from synthetic and spectroscopic results (Batten *et al.*, 1974; Johnson *et al.*, 1975). The structure of the title compound was postulated by the same authors to be that shown in Fig. 1. It seemed of interest to investigate its structure by means of X-ray crystallography as considerable deformation of the porphyrin macrocycle should occur. Also, the position of the Cl₂PdN₂ group in relation to the macrocycle and its shape were expected to be rather unusual.

Experimental. The sample was kindly supplied by the late Professor A. W. Johnson and Mr David Ward of Sussex University, England. The material was recrystallized by diffusion of petroleum ether (40–60°C) vapours into a chloroform solution of the complex in a closed system. Black crystals, irregular plates, max. thickness 0.05 mm; preliminary oscillation and Weissenberg equi-inclination photographs for levels 0–2 for all three directions; crystal cut from plate *ca* 0.05 × 0.05 × 0.5 mm, CAD-4 diffractometer (graphite monochromator). 15 reflections for measuring lattice parameters. 2908 reflections measured in Regional Laboratory of Physicochemical Measurements,

Jagiellonian University, Cracow, Poland; 2442 with $F_o \geq 3\sigma(F_o)$; no absorption correction; max. $2\theta = 81^\circ$, max. $hkl = 14,30,23$. Structure solved by heavy-atom method and refined anisotropically by difference Fourier synthesis and blocked full-matrix least-squares techniques (SHELX76; Sheldrick, 1976). Final refinements using F magnitudes converged with $R = 0.065$, $wR = 0.053$, $w = 1.6968/[\sigma^2(F_o) + 0.000394 F_o^2]$; $(\Delta/\sigma)_{\max} = -0.14$ for x coordinate of atom C(3); all H atoms except H(37) were found in a difference Fourier synthesis or calculated, and were treated as fixed contributions to structure-factor calculations and not refined. Position of H(37) was initially easily found from difference Fourier synthesis and positional parameters but no isotropic temperature factor was refined. C(37)–H(37) bond length of 1.295 Å [Pd...H(37) = 2.315 (4) Å] suggested that the H(37) might have moved into the residual diffraction ripple around the Pd atom. Therefore, a final difference Fourier synthesis was again calculated at the end of refinement and the position of H(37) was found as the largest peak of $0.56 e \text{ \AA}^{-3}$. All calculations with SHELX76 (Sheldrick, 1976) and XANADU (Roberts & Sheldrick, 1975) on IBM 370/165 and ODR A 1305; scattering factors as incorporated in SHELX76 and for Pd from *International Tables for X-ray Crystallography* (1974).

Discussion. Fig. 1 shows the molecular structure assigned to the compound by Johnson and co-workers [Johnson, Ward, Batten, Hamilton, Shelton & Elson, 1975, p. 2079, Fig. (IX)]. The molecular structure as found in the present work and the atomic nomenclature are shown in Fig. 2. Fig. 3 shows the deviations of the porphyrin ring and bridging atoms from the mean plane defined by the N(21)–N(24) atoms. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. Intramolecular bond distances and angles are given in Table 2.*

As Fig. 2 shows, the ethoxycarbonylmethylene group and PdCl₂ do not bridge the same pair of pyrrole nitrogen atoms as postulated by Johnson *et al.* [1975, p. 2079, Fig. (IX)], Fig. 1, but two opposite pairs of *cis* pyrrole N atoms. The introduction of the carbon atom between N(23) and N(24) together with the bridging of N(21) and N(22) by the Pd atom completes two new six-membered rings within the porphyrin core. The resulting structure is considerably folded (Fig. 3). The N(21) and N(22) pyrrole rings deviate in the opposite direction to the N(23) and N(24) pyrrole rings from the mean plane defined by the four nitrogen atoms. This

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares planes information have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42045 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

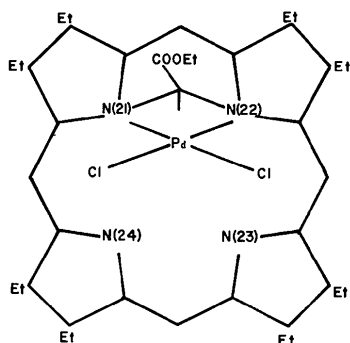


Fig. 1. The structure as postulated by Johnson, Ward, Batten, Hamilton, Shelton & Elson [1975, p. 2079, Fig. (IX)].

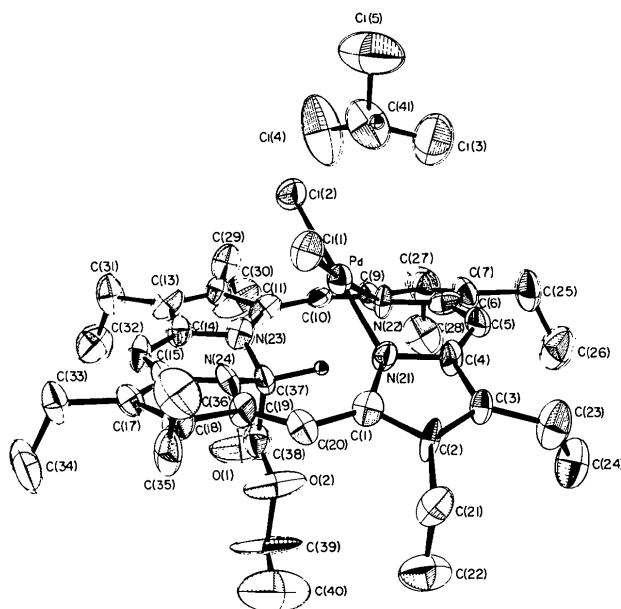


Fig. 2. The molecular structure and atomic nomenclature. Thermal ellipsoids are drawn at the 50% probability level.

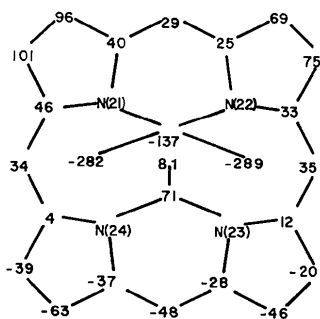


Fig. 3. Deviations of the porphyrin ring and bridging atoms from the mean plane defined by the four pyrrole nitrogen atoms N(21), N(22), N(23) and N(24) in Å × 100. E.s.d.'s are (Å) 0.001 for Pd, 0.003 for Cl, 0.009 for N, 0.01 for C atoms in the porphyrin core, 0.02 for the bridging C(37) atom and 0.13 for H(37).

results from the necessity to accommodate PdCl₂ and CHCO₂C₂H₅ in the middle of the porphyrin macrocycle. This bending of the macrocycle occurs roughly along the line passing through C(11) and C(19) and not C(10) and C(23) as was observed in the similar single *cis-N,N'*-bridged structure of ethoxycarbonyloctaethylmethanoporphyrin hydrobromide (Bartczak, 1985). Inspection of Fig. 3 shows also that the N(21) and N(22) pyrrole rings are additionally bent along C_α...C_α, whereas the N(23) and N(24) pyrrole rings are puckered. The bridging by Pd and C(37) and their out-of-plane positions (Fig. 3) cause all four pyrrole N atoms to be slightly tetrahedrally distorted. The appropriate sums of angles around these N atoms are

Table 1. Fractional atomic coordinates (× 10⁵ for Pd, × 10⁴ for other atoms) and equivalent U values (Å² × 10³) for the non-hydrogen atoms

E.s.d.'s for U_{eq} are 0.001–0.002 Å².

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U _{eq}
Pd	43534 (6)	10642 (3)	26235 (4)	37
Cl(1)	4275 (2)	1695 (1)	1834 (2)	51
Cl(2)	3508 (2)	529 (1)	2032 (2)	50
N(21)	5074 (6)	1488 (3)	3179 (5)	37
N(22)	4693 (5)	529 (3)	3299 (5)	37
N(23)	2778 (6)	887 (4)	3616 (5)	42
N(24)	3098 (7)	1745 (3)	3458 (5)	36
C(1)	5051 (8)	1998 (4)	3363 (6)	38
C(2)	5866 (7)	2164 (5)	3492 (7)	48
C(3)	6369 (8)	1760 (5)	3418 (6)	37
C(4)	5876 (8)	1338 (5)	3252 (7)	41
C(5)	6075 (8)	828 (5)	3206 (6)	42
C(6)	5523 (8)	444 (4)	3308 (5)	41
C(7)	5655 (10)	-60 (4)	3556 (6)	46
C(8)	4962 (9)	-281 (5)	3721 (7)	45
C(9)	4336 (10)	111 (4)	3578 (6)	40
C(10)	3536 (10)	36 (5)	3728 (6)	46
C(11)	2862 (8)	349 (4)	3696 (6)	42
C(12)	2033 (8)	146 (5)	3690 (6)	37
C(13)	1489 (9)	537 (5)	3610 (6)	52
C(14)	1933 (7)	982 (4)	3588 (6)	39
C(15)	1695 (7)	1494 (5)	3485 (6)	43
C(16)	2300 (9)	1876 (5)	3405 (6)	42
C(17)	2189 (8)	2380 (4)	3245 (6)	38
C(18)	2953 (9)	2583 (4)	3225 (7)	48
C(19)	3541 (9)	2189 (4)	3383 (6)	39
C(20)	4357 (9)	2299 (4)	3387 (5)	40
C(21)	6086 (8)	2695 (5)	3722 (7)	55
C(22)	5976 (9)	2773 (5)	4472 (8)	83
C(23)	7245 (9)	1738 (5)	3566 (8)	66
C(24)	7449 (9)	1507 (6)	4248 (7)	74
C(25)	6491 (9)	-279 (5)	3628 (8)	67
C(26)	6960 (10)	-101 (6)	4244 (9)	89
C(27)	4784 (9)	-784 (5)	4054 (7)	60
C(28)	4783 (10)	-748 (5)	4804 (8)	87
C(29)	1849 (8)	-411 (5)	3714 (7)	57
C(30)	1819 (11)	-618 (6)	4412 (9)	111
C(31)	565 (8)	510 (4)	3603 (7)	57
C(32)	217 (9)	590 (6)	4285 (7)	85
C(33)	1403 (8)	2653 (5)	3113 (7)	57
C(34)	1045 (10)	2872 (6)	3726 (9)	98
C(35)	3180 (8)	3117 (4)	3033 (8)	53
C(36)	3436 (9)	3161 (5)	2304 (8)	72
C(37)	3320 (7)	1288 (4)	3838 (7)	37
H(37)	3920	1170	3800	49
C(38)	3185 (9)	1392 (6)	4592 (7)	111
O(1)	2766 (8)	1156 (4)	4947 (5)	105
O(2)	3608 (8)	1768 (4)	4770 (5)	129
C(39)	3500 (14)	1938 (7)	5454 (7)	171
C(40)	3845 (15)	2414 (9)	5500 (11)	95
C(41)	4073 (11)	-709 (5)	1882 (8)	135
Cl(3)	4923 (3)	-1014 (2)	2222 (3)	135
Cl(4)	3245 (3)	-991 (2)	2175 (3)	158
Cl(5)	4154 (5)	-766 (2)	1022 (3)	168

356, 355, 354 and 354° (e.s.d.'s 1°) for N(21) to N(24) respectively. Similar distortions were observed, for example, in (1-3- η -allyl)(8,8'-dimethyl-2,2'-biquinoly)-palladium(II) (Deeming, Rothwell, Hursthouse & Backer-Dirks, 1979).

Table 2. *Interatomic distances (Å) and angles (°)*

N(21)-Pd	1.974 (10)	C(15)-C(14)	1.419 (16)
N(22)-Pd	2.029 (9)	C(37)-N(23)	1.454 (15)
Cl(1)-Pd	2.292 (3)	C(16)-C(15)	1.430 (18)
Cl(2)-Pd	2.312 (3)	C(17)-C(16)	1.376 (17)
C(1)-N(21)	1.393 (15)	N(24)-C(16)	1.372 (18)
C(4)-N(21)	1.395 (17)	C(18)-C(17)	1.378 (19)
C(20)-C(1)	1.398 (19)	C(19)-C(18)	1.457 (18)
C(2)-C(1)	1.444 (18)	N(24)-C(19)	1.390 (15)
C(3)-C(2)	1.361 (18)	C(37)-N(24)	1.467 (15)
C(4)-C(3)	1.417 (18)	C(38)-C(37)	1.546 (20)
C(5)-C(4)	1.387 (19)	H(37)-C(37)	1.05
C(6)-C(5)	1.380 (18)	O(1)-C(38)	1.169 (19)
C(7)-C(6)	1.432 (16)	O(2)-C(38)	1.265 (19)
N(22)-C(6)	1.394 (16)	C(39)-O(2)	1.446 (18)
C(8)-C(7)	1.330 (21)	C(40)-C(39)	1.382 (31)
C(9)-C(8)	1.491 (19)	C(21)-C(2)	1.514 (18)
N(22)-C(9)	1.369 (15)	C(22)-C(21)	1.520 (21)
C(10)-C(9)	1.373 (22)	C(23)-C(3)	1.482 (19)
C(11)-C(10)	1.390 (19)	C(24)-C(23)	1.528 (21)
C(12)-C(11)	1.475 (18)	C(26)-C(25)	1.526 (23)
N(23)-C(11)	1.431 (15)	C(27)-C(8)	1.509 (18)
C(29)-C(12)	1.499 (18)	C(28)-C(27)	1.500 (21)
C(13)-C(12)	1.379 (19)	C(30)-C(29)	1.496 (22)
C(14)-C(13)	1.383 (18)	C(31)-C(13)	1.534 (20)
N(23)-C(14)	1.424 (16)	C(32)-C(31)	1.492 (20)
C(33)-C(17)	1.511 (18)	C(20)-C(19)	1.382 (20)
C(34)-C(33)	1.476 (22)	Cl(3)-C(41)	1.758 (17)
C(35)-C(18)	1.506 (17)	Cl(4)-C(41)	1.666 (18)
C(36)-C(35)	1.520 (21)	Cl(5)-C(41)	1.728 (17)
Cl(2)-Pd-Cl(1)	93.2 (1)	C(5)-C(4)-C(3)	130 (1)
N(21)-Pd-Cl(1)	90.6 (3)	C(6)-C(5)-C(4)	123 (1)
N(21)-Pd-Cl(2)	176.1 (3)	C(7)-C(6)-C(5)	129 (1)
N(22)-Pd-Cl(1)	167.1 (3)	N(22)-C(6)-C(5)	122 (1)
N(22)-Pd-Cl(2)	94.9 (3)	N(22)-C(6)-C(7)	108 (1)
N(22)-Pd-N(21)	81.5 (4)	C(25)-C(7)-C(6)	122 (1)
C(1)-N(21)-Pd	132.6 (8)	C(8)-C(7)-C(6)	111 (1)
C(4)-N(21)-Pd	118.4 (8)	C(8)-C(7)-C(25)	127 (1)
C(4)-N(21)-C(1)	106 (1)	C(27)-C(8)-C(7)	131 (1)
C(2)-C(1)-N(21)	108 (1)	C(9)-C(8)-C(7)	105 (1)
C(20)-C(1)-N(21)	125 (1)	C(9)-C(8)-C(27)	124 (1)
C(3)-C(2)-C(1)	109 (1)	N(22)-C(9)-C(8)	110 (1)
C(20)-C(1)-C(2)	126 (1)	C(10)-C(9)-C(8)	122 (1)
C(21)-C(2)-C(1)	124 (1)	C(10)-C(9)-N(22)	128 (1)
C(3)-C(2)-C(21)	127 (1)	C(6)-N(22)-Pd	113.2 (7)
C(4)-C(3)-C(2)	106 (1)	C(9)-N(22)-Pd	135.1 (8)
C(23)-C(3)-C(2)	127 (1)	C(9)-N(22)-C(6)	107 (1)
C(4)-C(3)-C(23)	126 (1)	C(11)-C(10)-C(9)	133 (1)
C(3)-C(4)-N(21)	111 (1)	C(12)-C(11)-C(10)	122 (1)
C(5)-C(4)-N(21)	120 (1)	N(23)-C(11)-C(10)	132 (1)
N(23)-C(11)-C(12)	106 (1)	C(20)-C(19)-N(24)	134 (1)
C(29)-C(12)-C(11)	123 (1)	C(19)-N(24)-C(16)	107 (1)
C(13)-C(12)-C(11)	110 (1)	C(37)-N(24)-C(16)	119 (1)
C(13)-C(12)-C(29)	127 (1)	C(37)-N(24)-C(19)	128 (1)
C(14)-C(13)-C(12)	107 (1)	C(19)-C(20)-C(1)	133 (1)
C(31)-C(13)-C(12)	128 (1)	N(24)-C(37)-N(23)	107 (1)
C(14)-C(13)-C(31)	125 (1)	C(38)-C(37)-N(23)	110 (1)
N(23)-C(14)-C(13)	112 (1)	C(38)-C(37)-N(24)	109 (1)
C(15)-C(14)-C(13)	131 (1)	H(37)-C(37)-N(23)	111
C(15)-C(14)-N(23)	117 (1)	H(37)-C(37)-N(24)	116
C(14)-N(23)-C(11)	105.9 (9)	H(37)-C(37)-C(38)	105
C(37)-N(23)-C(11)	129 (1)	O(1)-C(38)-C(37)	126 (1)
C(37)-N(23)-C(14)	119.5 (9)	O(2)-C(38)-C(37)	109 (1)
C(16)-C(15)-C(14)	119 (1)	O(2)-C(38)-O(1)	125 (1)
C(17)-C(16)-C(15)	128 (1)	C(39)-O(2)-C(38)	116 (1)
N(24)-C(16)-C(15)	119 (1)	C(40)-C(39)-O(2)	107 (1)
N(24)-C(16)-C(17)	113 (1)	C(22)-C(21)-C(2)	113 (1)
C(18)-C(17)-C(16)	105 (1)	C(24)-C(23)-C(3)	114 (1)
C(33)-C(17)-C(16)	128 (1)	C(26)-C(25)-C(7)	115 (1)
C(18)-C(17)-C(33)	127 (1)	C(28)-C(27)-C(8)	113 (1)
C(19)-C(18)-C(17)	110 (1)	C(30)-C(29)-C(12)	113 (1)
C(35)-C(18)-C(17)	127 (1)	C(32)-C(31)-C(13)	112 (1)
C(19)-C(18)-C(35)	124 (1)	C(34)-C(33)-C(17)	113 (1)
N(24)-C(19)-C(18)	106 (1)	C(36)-C(35)-C(18)	113 (1)
C(20)-C(19)-C(18)	120 (1)	Cl(4)-C(41)-Cl(3)	108.8 (9)
		Cl(5)-C(41)-Cl(3)	106.4 (9)
		Cl(5)-C(41)-Cl(4)	112 (1)

The particularly interesting feature of this structure is the distortion of the palladium square-planar coordination geometry caused by significant intramolecular bonding: Pd-H(37) = 2.47 Å. The Pd-H distance in Pd hydride was found by electronography to be 1.67 Å (Semiletov, Baranova, Khodyrev & Imanov, 1980). The Pd...C(37) contact is 3.03 (1) Å. This kind of coordination is very unusual as it represents a case of rare five coordination of Pd^{II}. It can best be described as distortion towards trigonal-bipyramidal coordination as the least-squares plane through Cl(1), Cl(2), N(21) and N(22) shows: Cl(1) and N(22) bend away from H(37). The deviations of atoms from the above plane are Cl(1) -0.090 (3), Cl(2) 0.085 (3), N(21) 0.12 (1), N(22) -0.11 (1), Pd 0.087 (2), H(37) 1.98 Å. A somewhat similar case of a five-coordinate Pd^{II} complex has been reported (Konietzny, Bailey & Maitlis, 1975). The case of Pd-H intramolecular bonding was described in *trans*-diiodobis(dimethylphenylphosphine)palladium(II) (Bailey, Jenkins, Mason & Shaw, 1965). The Pd-H distance (H on the β carbon of the phenyl ring of the phosphine) was calculated as 2.8 Å.

The plane N(21)-Pd-N(22) forms an angle of 64.3 (5)° with the mean plane of the four pyrrole rings. The deviations of the two Cl atoms from this plane are -0.405 (4) and 0.045 (3) Å. The N-Pd-N plane forms an angle of 10.18 (5)° with the Cl(1)-Pd-Cl(2) plane (Table 3, deposited). The Pd-N distances [1.974 (10) and 2.029 (9) Å] are equal within 3 σ and in accordance with the values found in Pd(5,10,15,20-tetraphenylporphyrin) [2.009 (9) Å, Fleischer, Miller & Webb, 1964] and in the *A/D*-secocorrinoid complex of Pd^{II} (2.01-2.02 Å, Currie & Dunitz, 1971). These distances as well as the Pd-Cl(1) = 2.292 (3) and Pd-Cl(2) = 2.312 (3) Å bond lengths are in good agreement with the rule that the Pd-Cl bond is sensitive to the nature of the *trans* atom and is shortest when Cl or N is the *trans* atom (Steffen & Palenik, 1976, Table XI). The ethoxycarbonylmethylene group shows some disorder as the shapes of the thermal ellipsoids of O(2), C(39) and C(40) indicate (Fig. 3), but much less pronounced than was observed in the structure of the *cis-N,N'*-ethoxycarbonylmethylene-substituted octaethylporphyrin hydrobromide (Bartczak, 1985). All but one of the ethyl terminal groups, C(35)-C(36), point in the same direction, which is opposite to the tilt of the Cl(1)-Pd-Cl(3) plane; this probably results from packing considerations. There is a well defined molecule of chloroform present in the asymmetric unit. The closest contacts made by its chlorine atoms are Cl(3)...H(271) = 2.95, Cl(3)...H(361) = 2.86, Cl(4)...H(352) = 2.95 Å.

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References

- BAILEY, N. A., JENKINS, J. M., MASON, R. & SHAW, B. L. (1965). *J. Chem. Soc. Chem. Commun.* pp. 237–238.
- BARTCZAK, T. J. (1985). *Acta Cryst.* **C41**, 604–607.
- BATTEN, P., HAMILTON, A., JOHNSON, A. W., SHELTON, W. & WARD, D. (1974). *J. Chem. Soc. Chem. Commun.* pp. 550–551.
- CURRIE, M. & DUNITZ, J. D. (1971). *Helv. Chim. Acta*, **54**, 98–112.
- DEEMING, A. J., ROTHWELL, I. P., HURSTHOUSE, M. B. & BACKER-DIRKS, J. D. J. (1979). *J. Chem. Soc. Chem. Commun.* pp. 670–672.
- FLEISCHER, E. B., MILLER, C. K. & WEBB, L. E. (1964). *J. Am. Chem. Soc.* **86**, 2342–2347.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, A. W., WARD, D., BATTEN, P., HAMILTON, A. L., SHELTON, G. & ELSON, C. M. (1975). *J. Chem. Soc. Perkin Trans. 1*, pp. 2076–2085.
- KONIECZY, A., BAILEY, P. M. & MAITLIS, P. M. (1975). *J. Chem. Soc. Chem. Commun.* pp. 78–79.
- ROBERTS, P. & SHELDRIK, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.
- SEMILETOV, S. A., BARANOVA, R. V., KHODYREV, YU. P. & IMANOV, R. M. (1980). *Kristallografiya*, **25**, 1162–1168.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- STEFFEN, W. L. & PALENIK, G. J. (1976). *Inorg. Chem.* **15**, 2432–2439.

Acta Cryst. (1985). **C41**, 869–871

Structure of (*N,N*-Dimethylbenzylamino-*N,C*)iodo(4-methoxyphenyl)-(4-methylphenyl)lead(IV), [PbI(C₇H₇)(C₉H₁₂N)(C₇H₇O)]

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Abstract. $M_r = 666.56$, monoclinic, $P2_1/n$, $a = 10.994$ (3), $b = 12.491$ (2), $c = 16.715$ (4) Å, $\beta = 94.87$ (2)°, $V = 2287$ (1) Å³, $Z = 4$, $D_x = 1.936$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71073$ Å, $\mu = 87.8$ cm⁻¹, $F(000) = 1256$, room temperature, final $R = 0.0283$ for 2129 significant reflexions. The lead atom is five-coordinated by iodine, nitrogen and three carbon atoms in a distorted trigonal bipyramidal geometry with bond lengths Pb–I 2.956 (1), Pb–N 2.685 (7), Pb–C 2.186 (7), 2.206 (7), 2.209 (8) Å. Iodine and nitrogen atoms are apical. The three carbon atoms are equatorial with the lead atom slightly out of their plane in the direction of the iodine atom.

Introduction. The title compound was the first chiral triorganolead compound synthesized (van der Kooi, Wolters & van der Gen, 1979). An X-ray structure determination was made to confirm the supposed geometry and to explain the PMR behaviour of the compound. Although this compound has much in

common with bromo(*N,N*-dimethylbenzylamino-*N,C*)diphenyltin bromide (van Koten, Noltes & Spek, 1976), the structures are not isomorphous. The synthesis of the title compound was described in the paper by van der Kooi *et al.* (1979). Initial results of the structure determination were mentioned in that paper. However, the lattice constants are corrected and the numerical values of distances and angles differ slightly from those in the previous paper. The differences are small and have no bearing on the conclusions given by van der Kooi *et al.* (1979) (*e.g.* the PMR behaviour).

Experimental. Crystal dimensions $0.40 \times 0.15 \times 0.10$ mm; for source of material see van der Kooi *et al.* (1979); Enraf–Nonius CAD-4 four-circle diffractometer; graphite-monochromated $Mo K\alpha$; cell constants from setting angles of 24 reflexions; absorption correction applied, transmission varying from 0.47 to 0.59; $\theta_{max} = 30^\circ$; standard reflexions revealed loss in intensity of 16%, polynomial correction applied; overall e.s.d.'s of standard reflexions between 0.012 and 0.018; 7294 reflexions measured, of which 6593 independent,

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