Structure of Dichloro(phthalocyaninato)niobium(IV)

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Abstract. $C_{32}H_{16}Cl_2N_8Nb$, [$NbCl_2(pc)$], $M_r = 676.34$, monoclinic, $P2_1/c$, $a = 12.557$ (2), $b = 10.315$ (2), $c = 20.571$ (7) Å, $\beta = 90.59$ (2)°, $V = 2664.3$ Å^3, $Z = 4$, $D_c = 1.686$ g cm^{-3}, $\mu(Cu\ K\alpha) = 59.8$ cm^{-1}; final $R_w = 0.038$ for 4049 reflections with $|F_o| > 3\sigma(F)$. The Nb atom is coordinated to four isoindole N atoms and two Cl atoms, and is displaced 0.98 Å from the central C_8N_8 plane.

Introduction. The synthesis and properties of niobium–phthalocyanine powder were reported by Buslaev, Kuznetsova & Goryachova (1967). As part of synthetic studies of quasi one-dimensional metals, the preparation of single crystals was undertaken. However, single-crystal X-ray diffraction studies showed the crystal to be dichloro(phthalocyaninato)niobium(IV).

Niobium pentachloride and phthalonitrile were allowed to react in quinoline for 4 h at 490 K in a pure argon atmosphere. Single crystals precipitated when the reaction mixture was cooled to room temperature. The crystals were then kept at 570 K for 40 h in a stream of pure argon at about 3 × 10^2 Pa to remove the impurities occluded in them.

Intensity data were collected from a single crystal (0.2 × 0.2 × 0.3 mm) on a computer-controlled four-circle diffractometer (Rigaku AFC-6A) using graphite-monochromated Cu $K\alpha$ radiation. 4688 independent reflections were measured in the range $2\theta \le 135°$; 4049 of these were used for structure determination [$|F_o| > 3\sigma(F)$]. No correction was made for absorption. Cell dimensions were determined from the setting angles of 16 reflections with $55 < 2\theta < 60°$.

All calculations were performed with the *UNICS* III program system (Sakurai & Kobayashi, 1979). The structure was solved by direct methods, using a modified version of the program *LSAM* (Main, Woolfson & Germain, 1972). The solution with the largest figure of merit led to an E map which was readily interpreted in terms of a reasonable structure, although a few false peaks were present. Isotropic refinement converged to an R of 0.097. Anisotropic refinement resulted in an R of 0.042. A difference Fourier synthesis revealed the positions of all the H atoms in the molecule. The coordinates of the H atoms

were adjusted by assuming a C—H distance of 0.91 Å. These positional parameters together with isotropic thermal parameters equal to those of the atoms to

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* (Å^2)

$$B_{eq} = \tfrac{4}{3} \sum_i \sum_j B_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}
Nb	2244.2 (4)	2127.2 (5)	191.1 (2)	2.5
Cl(1)	3127 (1)	4173 (2)	342 (1)	4.5
Cl(2)	2871 (1)	2472 (2)	−898 (1)	4.7
N(1)	4071 (3)	−328 (4)	581 (2)	2.7
N(2)	3066 (3)	1457 (4)	1035 (2)	2.6
N(3)	2436 (3)	2935 (5)	1860 (2)	3.1
N(4)	1227 (3)	2906 (5)	938 (2)	2.8
N(5)	−331 (3)	3393 (4)	283 (2)	3.0
N(6)	709 (3)	1666 (4)	−207 (2)	2.8
N(7)	1123 (3)	−159 (5)	−905 (2)	3.1
N(8)	2503 (3)	143 (4)	−80 (2)	2.7
C(1)	3886 (4)	543 (5)	1035 (3)	2.7
C(2)	4458 (4)	609 (5)	1635 (3)	2.9
C(3)	5341 (5)	−62 (6)	1871 (3)	3.6
C(4)	5664 (5)	142 (6)	2496 (3)	4.1
C(5)	5107 (5)	1007 (6)	2887 (3)	4.0
C(6)	4237 (5)	1691 (6)	2659 (3)	3.4
C(7)	3934 (4)	1504 (5)	2027 (3)	2.9
C(8)	3082 (4)	2032 (6)	1643 (2)	2.8
C(9)	1614 (4)	3360 (5)	1531 (3)	3.0
C(10)	920 (4)	4413 (6)	1754 (3)	3.3
C(11)	1001 (5)	5235 (6)	2274 (3)	3.8
C(12)	236 (5)	6194 (6)	2314 (3)	4.3
C(13)	−599 (5)	6287 (6)	1875 (3)	4.2
C(14)	−695 (5)	5448 (6)	1362 (3)	3.7
C(15)	99 (4)	4519 (6)	1295 (3)	3.2
C(16)	297 (4)	3570 (5)	794 (3)	2.9
C(17)	−170 (4)	2498 (5)	−157 (3)	2.9
C(18)	−909 (4)	2177 (6)	−678 (3)	3.0
C(19)	−1881 (4)	2724 (6)	−875 (3)	3.8
C(20)	−2393 (4)	2211 (7)	−1410 (3)	4.3
C(21)	−1992 (5)	1160 (7)	−1736 (3)	4.4
C(22)	−1046 (5)	590 (6)	−1545 (3)	3.8
C(23)	−500 (4)	1119 (6)	−1016 (3)	3.2
C(24)	515 (4)	815 (6)	−713 (3)	3.1
C(25)	2019 (4)	−466 (5)	−612 (3)	2.9
C(26)	2664 (4)	−1567 (6)	−804 (3)	3.1
C(27)	2531 (5)	−2487 (6)	−1294 (3)	4.1
C(28)	3282 (5)	−3442 (7)	−1331 (3)	5.2
C(29)	4138 (5)	−3493 (6)	−892 (3)	4.8
C(30)	4288 (4)	−2603 (6)	−401 (3)	3.6
C(31)	3524 (4)	−1604 (5)	−369 (3)	2.9
C(32)	3422 (4)	−538 (5)	84 (3)	2.7

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which the H atoms are bonded were included in the final refinement but not refined. The least-squares

Table 2. *Bond lengths* (Å) *and angles* (°)

Nb—Cl(1)	2·403 (2)	Nb—Cl(2)	2·409 (2)
Nb—N(2)	2·125 (4)	Nb—N(4)	2·162 (4)
Nb—N(6)	2·140 (4)	Nb—N(8)	2·148 (4)
N(1)—C(1)	1·319 (7)	N(1)—C(32)	1·319 (7)
N(2)—C(1)	1·397 (7)	N(2)—C(8)	1·385 (7)
N(3)—C(8)	1·316 (7)	N(3)—C(9)	1·305 (7)
N(4)—C(9)	1·391 (7)	N(4)—C(16)	1·383 (7)
N(5)—C(16)	1·321 (7)	N(5)—C(17)	1·310 (7)
N(6)—C(17)	1·403 (7)	N(6)—C(24)	1·383 (7)
N(7)—C(24)	1·323 (8)	N(7)—C(25)	1·311 (7)
N(8)—C(25)	1·394 (7)	N(8)—C(32)	1·389 (7)
C(1)—C(2)	1·424 (8)	C(2)—C(3)	1·390 (8)
C(2)—C(7)	1·395 (8)	C(3)—C(4)	1·362 (9)
C(4)—C(5)	1·394 (9)	C(5)—C(6)	1·379 (9)
C(6)—C(7)	1·366 (8)	C(7)—C(8)	1·431 (8)
C(9)—C(10)	1·469 (8)	C(10)—C(11)	1·367 (9)
C(10)—C(15)	1·396 (8)	C(11)—C(12)	1·382 (9)
C(12)—C(13)	1·381 (9)	C(13)—C(14)	1·369 (9)
C(14)—C(15)	1·390 (8)	C(15)—C(16)	1·445 (8)
C(17)—C(18)	1·449 (8)	C(18)—C(19)	1·401 (9)
C(18)—C(23)	1·394 (8)	C(19)—C(20)	1·374 (9)
C(20)—C(21)	1·373 (10)	C(21)—C(22)	1·379 (9)
C(22)—C(23)	1·393 (9)	C(23)—C(24)	1·447 (8)
C(25)—C(26)	1·453 (8)	C(26)—C(27)	1·393 (9)
C(26)—C(31)	1·396 (8)	C(27)—C(28)	1·366 (9)
C(28)—C(29)	1·398 (10)	C(29)—C(30)	1·376 (9)
C(30)—C(31)	1·410 (8)	C(31)—C(32)	1·449 (8)

Cl(1)—Nb—Cl(2)	80·6 (1)	Cl(1)—Nb—N(2)	87·7 (1)
Cl(1)—Nb—N(4)	81·8 (1)	Cl(2)—Nb—N(6)	88·8 (1)
Cl(2)—Nb—N(8)	81·2 (1)	N(2)—Nb—N(4)	80·0 (2)
N(2)—Nb—N(8)	80·2 (2)	N(4)—Nb—N(6)	79·5 (2)
N(6)—Nb—N(8)	80·0 (2)	C(1)—N(1)—C(32)	123·3 (5)
Nb—N(2)—C(1)	124·9 (3)	Nb—N(2)—C(8)	127·0 (4)
C(1)—N(2)—C(8)	106·6 (4)	C(8)—N(3)—C(9)	123·3 (5)
Nb—N(4)—C(9)	123·0 (3)	Nb—N(4)—C(16)	122·4 (3)
C(9)—N(4)—C(16)	107·9 (5)	C(16)—N(5)—C(17)	123·5 (5)
Nb—N(6)—C(17)	122·9 (3)	Nb—N(6)—C(24)	125·5 (3)
C(17)—N(6)—C(24)	108·1 (5)	C(24)—N(7)—C(25)	122·8 (5)
Nb—N(8)—C(25)	124·6 (3)	Nb—N(8)—C(32)	123·1 (3)
C(25)—N(8)—C(32)	108·5 (4)	N(1)—C(1)—N(2)	126·6 (5)
N(1)—C(1)—C(2)	123·8 (5)	N(2)—C(1)—C(2)	109·5 (5)
C(1)—C(2)—C(3)	132·2 (5)	C(1)—C(2)—C(7)	107·2 (5)
C(3)—C(2)—C(7)	120·5 (5)	C(2)—C(3)—C(4)	118·8 (6)
C(3)—C(4)—C(5)	119·9 (6)	C(4)—C(5)—C(6)	122·1 (6)
C(5)—C(6)—C(7)	117·6 (6)	C(2)—C(7)—C(6)	121·1 (5)
C(2)—C(7)—C(8)	106·8 (5)	C(6)—C(7)—C(8)	132·1 (5)
N(2)—C(8)—N(3)	127·3 (5)	N(2)—C(8)—C(7)	109·8 (5)
N(3)—C(8)—C(7)	122·9 (5)	N(3)—C(9)—N(4)	127·6 (5)
N(3)—C(9)—C(10)	123·7 (5)	N(4)—C(9)—C(10)	108·7 (5)
C(9)—C(10)—C(11)	131·6 (6)	C(9)—C(10)—C(15)	106·4 (5)
C(11)—C(10)—C(15)	121·9 (6)	C(10)—C(11)—C(12)	116·4 (6)
C(11)—C(12)—C(13)	122·3 (6)	C(12)—C(13)—C(14)	121·4 (6)
C(13)—C(14)—C(15)	117·1 (6)	C(10)—C(15)—C(14)	120·8 (5)
C(10)—C(15)—C(16)	107·4 (5)	C(14)—C(15)—C(16)	131·8 (5)
N(4)—C(16)—N(5)	126·8 (5)	N(4)—C(16)—C(15)	109·5 (5)
N(5)—C(16)—C(15)	123·8 (5)	N(5)—C(17)—N(6)	127·5 (5)
N(5)—C(17)—C(18)	124·7 (5)	N(6)—C(17)—C(18)	107·7 (5)
C(17)—C(18)—C(19)	132·2 (6)	C(17)—C(18)—C(23)	108·1 (5)
C(19)—C(18)—C(23)	119·7 (6)	C(18)—C(19)—C(20)	118·4 (6)
C(19)—C(20)—C(21)	121·6 (6)	C(20)—C(21)—C(22)	121·1 (6)
C(21)—C(22)—C(23)	118·1 (6)	C(18)—C(23)—C(22)	121·0 (6)
C(18)—C(23)—C(24)	106·5 (5)	C(22)—C(23)—C(24)	132·5 (6)
N(6)—C(24)—N(7)	127·5 (5)	N(6)—C(24)—C(23)	109·5 (5)
N(7)—C(24)—C(23)	123·0 (5)	N(7)—C(25)—N(8)	128·1 (5)
N(7)—C(25)—C(26)	122·8 (5)	N(8)—C(25)—C(26)	109·1 (5)
C(25)—C(26)—C(27)	131·8 (5)	C(25)—C(26)—C(31)	106·0 (5)
C(27)—C(26)—C(31)	122·1 (5)	C(26)—C(27)—C(28)	116·9 (6)
C(27)—C(28)—C(29)	121·3 (6)	C(28)—C(29)—C(30)	123·2 (6)
C(29)—C(30)—C(31)	115·7 (6)	C(26)—C(31)—C(30)	120·9 (5)
C(26)—C(31)—C(32)	108·6 (5)	C(30)—C(31)—C(32)	130·5 (5)
N(1)—C(32)—N(8)	127·7 (5)	N(1)—C(32)—C(31)	124·4 (5)
N(8)—C(32)—C(31)	107·8 (5)		

refinement converged to $R = 0.042$ and $R_w = 0.038$ [$w = \sigma^{-2}(F)$]. The largest peak on the final difference map was 0.6 e Å^{-3}. The final parameters are given in Table 1.* Atomic scattering factors and anomalous-dispersion corrections were obtained from *International Tables for X-ray Crystallography* (1974).

Discussion. The thermal ellipsoids, with the atom labelling, are presented in Fig. 1, and the molecular packing is shown in Figs. 2 and 3.

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* Lists of structure factors, anisotropic thermal parameters and details of a mean plane have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36530 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
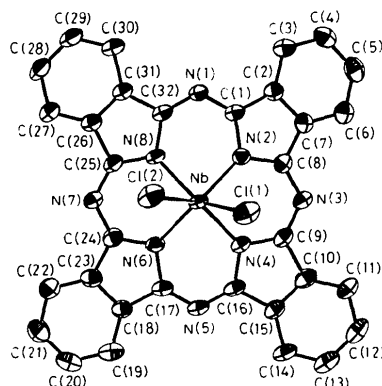
Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the [NbCl₂(pc)] molecule with 50% probability thermal ellipsoids.
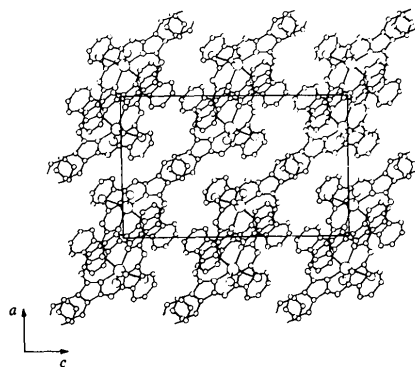
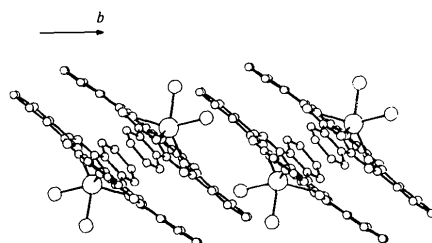Fig. 2. Packing of molecules in the unit cell viewed along the *b* axis.

Fig. 3. Stacking of molecules parallel to the *b* axis.

The central C_8N_8 ring is approximately planar, but is not coplanar with the benzene rings.* Displacement of Nb from the central C_8N_8 plane may be compared with the values of the out-of-plane displacement for oxoacetato($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)niobium (Lecomte, Protas, Guilard, Fliniaux & Fournari, 1976) (1·0 Å) and tri-μ-oxo-bis[($\alpha,\beta,\gamma,\delta$-tetraphenylporphinato)niobium] (Johnson & Scheidt, 1978) (1·02, 1·00 Å).

Bond distances and angles are listed in Table 2. The Nb—Cl distances are longer than those for the non-bridging Nb—Cl bonds in $NbCl_5$ (Zalkin & Sands, 1958) (2·250, 2·302 Å), $NbOCl_3$ (Sands, Zalkin & Elson, 1959) (2·24 Å), $NbCl_5POCl_3$ (Brändén & Lindqvist, 1963) (2·25 ~ 2·35 Å) and $NbCl_4F$ (Preiss, 1968) (2·26 ~ 2·31 Å). This indicates an ionic component in the Nb—Cl bonds of $[NbCl_2(pc)]$.

We thank M. Nakayama and T. Hori (Rigaku Corp., Tokyo) for the collection of the four-circle diffractometer data. Useful comments from Dr Y. Matsuda were appreciated.

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* See previous footnote.

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Bromotris[tetracarbonyl(triphenylphosphine)manganio]tin(IV)

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Abstract. $[SnBr\{Mn(C_{18}H_{15}P)(CO)_4\}_3]$, $C_{66}H_{45}BrMn_3O_{12}P_3Sn$, $M_r = 1486\cdot4$, triclinic, $P\bar{1}$, $a = 13\cdot515$ (3), $b = 22\cdot709$ (4), $c = 11\cdot004$ (3) Å, $\alpha = 86\cdot15$ (10), $\beta = 90\cdot05$ (10), $\gamma = 108\cdot33$ (10)°, $U = 3198$ Å^3, $Z = 2$, $D_c = 1\cdot544$ Mg m^{-3}, $F(000) = 1484$, Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å, μ(Mo $K\alpha$) = 1·6 mm^{-1}. Final $R = 0\cdot057$ for 8333 unique diffractometer data ($I > 3\sigma$) and 105 refined parameters. The three $Mn[(C_6H_5)_3P](CO)_4$ groups and the Br atom form a distorted tetrahedron round the Sn atom with Sn—Mn distances 2·727 (1), 2·718 (1), 2·708 (1) Å and Sn—Br 2·615 (1) Å.

Introduction. In the course of our investigations on the influence of packing forces in molecular crystals on the geometry of the molecules we have now prepared the compound $\{SnBr\{Mn[(C_6H_5)_3P](CO)_4\}_3\}$ and determined the crystal structure. The red crystals were prepared by reaction of $SnBr_2$ with $[Mn_2\{(C_6H_5)_3P\}_2(CO)_8]$ in 1,2,3,4-tetrahydronaphthalene at 403 K in a Schlenk tube at atmospheric pressure (Haupt & Schwab, 1978).

Data were collected with a crystal 0·38 × 0·46 × 0·69 mm. Cell parameters were determined by a least-squares procedure from the diffractometer angles of 15 reflexions measured with a Hilger & Watts Y 290 automatic four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation and a scintillation counter. The intensities of 9500 reflexions ($I > 3\sigma$) with $2 \le \theta \le 24\cdot6°$ were measured by the $\omega/2\theta$ scan technique, with a scan width $\Delta 2\theta$ (°) = 1·34 + 0·34 tan θ from background to background and a scan speed of 0·02°