

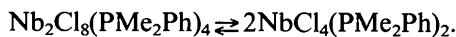
Table 6. Bond distances (Å) in niobium(IV) chloro phosphine complexes

	Nb—Cl ( <i>trans</i> to Cl)	Nb—Cl ( <i>trans</i> to P)	Nb—P
[NbCl <sub>6</sub> ] <sup>2-</sup>	2.409 [9]	—	—
[NbCl <sub>5</sub> (PMe <sub>2</sub> Ph)] <sup>-</sup>	2.363 [2]*	2.405 (5)	2.673 (5)
<i>trans</i> -NbCl <sub>4</sub> (PEt <sub>3</sub> ) <sub>2</sub> †	2.366 [9]	—	2.664 (3)
<i>trans</i> -NbCl <sub>4</sub> (PEtPh <sub>2</sub> ) <sub>2</sub> †	2.367 [34]	—	2.706 (1)

\* Averaged over only three Nb—Cl distances as explained in text.

† Cotton, Duraj & Roth (1984).

Roth, 1984) had shown that in a solution of Nb<sub>2</sub>Cl<sub>8</sub>(PMe<sub>2</sub>Ph)<sub>4</sub> there is a dissociation equilibrium,



We had hoped to obtain crystals of the monomer by employing dilute solutions. However, as noted in *Experimental* we obtained instead the ionic compound (PMe<sub>2</sub>PhH)[NbCl<sub>5</sub>(PMe<sub>2</sub>Ph)]. Presumably, over the time required for crystal growth some hydrolysis occurred, giving HCl, which reacted with NbCl<sub>4</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> to give the ionic product.

The present results can be compared with those for a few other quasi-octahedral Nb<sup>IV</sup> chloro complexes. Table 6 summarizes bond lengths for the present compounds and two other phosphine complexes (Cotton, Duraj & Roth, 1984). For *cis*-NbCl<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>, Nb—Cl distances in the range 2.328 (2) and 2.349 (4) Å have been found (Benton, Drew, Hobson & Rice, 1981).

The bond lengths in Table 6 are internally consistent. There are several small differences, but each one seems to have a straightforward explanation. The longest Nb—P distance is found for the least basic phosphine. There is a distinct *trans* effect from the phosphine in the [NbCl<sub>5</sub>(PMe<sub>2</sub>Ph)]<sup>-</sup> ion, with the *trans* Nb—Cl bond being 0.042 (5) Å longer than the *cis* bonds, excluding from consideration the Nb—Cl(3) bond which appears to be lengthened by hydrogen bonding with the P—H bond of the cation. Finally, we note that in the NbCl<sub>6</sub><sup>2-</sup> ion the Nb—Cl bonds are somewhat longer than those in the complexes with one or two neutral ligands, in keeping with the probable ionic character of these bonds, whereby the more of them there are to the same positive center, the weaker each one will become.

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## Structures of Three Bis(3-ethoxy-*N-R*-salicylideneaminato)nickel(II) Complexes (*R* = H, Methyl, Ethyl)

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**Abstract.** (I): Bis(3-ethoxysalicylideneaminato)nickel(II), [Ni(C<sub>9</sub>H<sub>10</sub>NO<sub>2</sub>)<sub>2</sub>], *M<sub>r</sub>* = 387.06, triclinic, *P*1̄, *a* = 11.906 (4), *b* = 10.089 (7), *c* = 8.442 (4) Å, *α* = 102.39 (4)°, *β* = 97.38 (3)°, *γ* = 111.18 (4)°, *V* = 899.54 Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1.45 (by flotation), *D<sub>x</sub>* = 1.43 Mg m<sup>-3</sup>, λ(Mo *Kα*) = 0.71069 Å, *μ* =

1.105 mm<sup>-1</sup>, *F*(000) = 404, room temperature, *R* = 0.034 for 3443 observed unique reflections. (II): Bis(3-ethoxy-*N*-methylsalicylideneaminato)nickel(II), [Ni(C<sub>10</sub>H<sub>12</sub>NO<sub>2</sub>)<sub>2</sub>], *M<sub>r</sub>* = 415.11, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 8.660 (3), *b* = 17.959 (6), *c* = 6.283 (3) Å, *β* = 97.13 (2)°, *V* = 969.64 Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1.41 (by flo-

Table 1. Details of data collection and refinement for (I), (II) and (III)

	(I)	(II)	(III)
Crystal form and size (mm)	Green prism 0.57 × 0.15 × 0.07	Green needle 0.37 × 0.23 × 0.04	Green needle 0.43 × 0.12 × 0.05
Radiation	Mo Kα	Mo Kα	Cu Kα
Reflections for cell parameters	16 (2θ ≥ 10°)	18 (2θ ≥ 8°)	20 (2θ ≥ 20°)
Scan speed	0.04	0.04	0.04
Scan width (°)	1.2	1.2	1.6
Scan mode	θ-2θ	θ-2θ	θ-2θ
2θ <sub>max</sub> (°)	60	60	140
Maximum values of indices			
<i>h</i>	-16→16	-11→12	-10→10
<i>k</i>	-13→12	0→23	0→30
<i>l</i>	0→11	0→8	0→5
Standard reflections	102 121 112	400 131 060	131 060 160
Variation (%)	3.4	2.2	4.1
<i>R</i>	0.034	0.036	0.044
<i>wR</i>	0.041	0.037	0.052
Weighting scheme	<i>k</i> = 0.0863	<i>k</i> = 1.0650	<i>k</i> = 0.5655
<i>w</i> = <i>k</i> / [σ <sup>2</sup> ( <i>F<sub>o</sub></i> ) + <i>g</i>   <i>F<sub>o</sub></i>   <sup>2</sup> ]	<i>g</i> = 0.012898	<i>g</i> = 0.000000	<i>g</i> = 0.008557
Independent measured reflections	3591	1318	1467
Observed reflections [ <i>I</i> > 3σ( <i>I</i> )]	3443	1161	1388
Refined parameters	232	146	155
Max. Δ/σ	0.142	0.006	0.027
Max. Δρ features (e Å <sup>-3</sup> )	-0.475 +0.617	-0.211 +0.308	-0.620 -0.277

tation),  $D_x = 1.42 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$ ,  $\mu = 1.028 \text{ mm}^{-1}$ ,  $F(000) = 436$ , room temperature,  $R = 0.036$  for 1161 reflections. (III): Bis(3-ethoxy-*N*-ethylsalicylideneaminato)nickel(II), [Ni(C<sub>11</sub>H<sub>14</sub>NO<sub>2</sub>)<sub>2</sub>],  $M_r = 443.16$ , monoclinic,  $P2_1/c$ ,  $a = 8.405$  (1),  $b = 25.256$  (6),  $c = 4.987$  (1) Å,  $\beta = 95.18$  (2)°,  $V = 1054.35 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_m = 1.39$  (by flotation),  $D_x = 1.40 \text{ Mg m}^{-3}$ ,  $\lambda(\text{Cu K}\alpha) = 1.5418 \text{ \AA}$ ,  $\mu = 1.547 \text{ mm}^{-1}$ ,  $F(000) = 468$ , room temperature,  $R = 0.044$  for 1388 reflections. All three complexes have molecular centres of symmetry and the Ni atoms in a square-planar coordination. The molecules have 'stepped' conformations with step heights 0.144 and 0.696 Å in two crystallographically independent molecules of (I), 0.514 Å in (II), and 0.616 Å in (III). The Ni—O bond lengths are similar in (I) [1.836 (1) and 1.846 (2) Å] and (III) [1.833 (2) Å] but shorter in (II) [1.815 (2) Å]. The Ni—N bond lengths have similar values in (II) [1.917 (3) Å] and (III) [1.921 (2) Å] but are significantly shorter in (I) [1.850 (2) and 1.851 (2) Å].

**Introduction.** The coordination around the Ni atom as well as the molecular conformation in bis(*N*-*R*-salicylideneaminato)nickel(II) complexes are dependent upon the N atom and benzene-ring substituents. Both tetrahedral (Fox, Orioli, Lingafelter & Sacconi, 1964; Braun & Lingafelter, 1967; Castellano, Hodder, Prout & Sadler, 1971) and square-planar coordination of the Ni atom have been found. Square-planar complexes adopt either completely planar (Stewart & Lingafelter, 1959; Fox & Lingafelter, 1967) or 'stepped' conformations (Frasson, Panattoni & Sacconi, 1959; Braun & Lingafelter, 1966; Shkol'nikova, Knyazeva & Voblikova, 1967; Bhatia, Bindlish, Saini & Jain,

1981; Bhatia, Syal, Kashyap, Jain & Brown, 1983; Jones, Waters, Kaitner & Kamenar, 1986; Fernández-G., Rosales, Toscano & Tapia T., 1986; Ravikumar, Rajan, Rajaram, Ramalingam & Natarajan, 1986; Britton & Pignolet, 1989) of the molecules. This effect was ascribed to both steric and electronic causes although the crystal packing forces must also be taken into account. In order to extend the existing data we have planned to determine or to redetermine the structures of a series of such complexes (Jones, Kaitner, Kamenar, Stefanović & Waters, 1985). We report here the structure determination of three complexes with an ethoxy substituent on the benzene ring at position 3 but with different *N* substituents,  $R = \text{H}$ ,  $\text{CH}_3$  and  $\text{C}_2\text{H}_5$ .

**Experimental.** Crystals by slow evaporation of dimethylformamide solutions. Crystal dimensions and data-collection procedures are given in Table 1. A Philips PW1100 diffractometer was used. Structures were solved by the heavy-atom method. Refinement was by the full-matrix least-squares method and with anisotropic thermal parameters. Function minimized  $\sum w(|F_o| - |F_c|)^2$  with weighting scheme given in Table 1. No absorption corrections. At the intermediate stage in the refinement, difference maps showed maxima in positions consistent with the expected locations of H atoms; in the final rounds of calculations H atoms were positioned on geometrical grounds (C—H = 1.08 Å) and included in the structure-factor calculations. Structure solutions and refinement were performed with *SHELX76* (Sheldrick, 1976), molecular-geometry calculations with *CSU* (*Crystal Structure Utility*) program (Vicković, 1988). Anomalous-scattering factors were from *International Tables for X-ray Cryst-*

*tallography* (1974). All calculations were carried out on a UNIVAC 1110 computer of the Zagreb University Computing Centre, SRCE.

**Discussion.** Final atomic coordinates are given in Table 2,\* bond lengths and angles in Table 3. The molecular structures of complexes (I), (II) and (III) are shown in Fig. 1. In all three structures the Ni atoms occupy the symmetry centres of the corresponding space groups thus realizing a *trans* planar arrangement around the Ni atoms. The complex molecules exhibit a 'stepped' conformation arising

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52849 (45 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

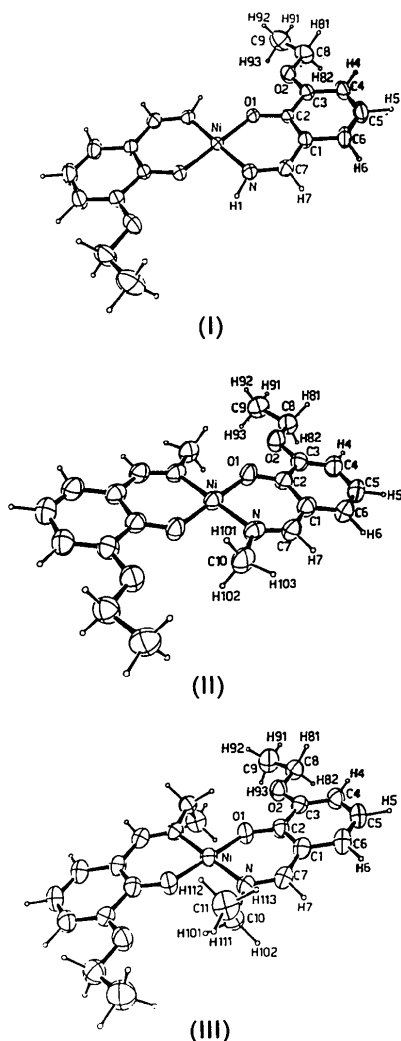


Fig. 1. ORTEP (Johnson, 1971) views of the molecular structures of (I), (II) and (III) showing the atom-numbering schemes. Ellipsoids are at 50% probability level.

Table 2. Final atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ )

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
(IA)				
Ni	0	0	0	267 (1)
O(1)	291 (2)	1371 (2)	1993 (2)	337 (3)
O(2)	1061 (2)	3660 (2)	4544 (2)	539 (5)
N	-1193 (2)	-1502 (2)	537 (2)	341 (4)
C(1)	-1221 (2)	-130 (3)	3231 (3)	360 (5)
C(2)	-275 (2)	1192 (3)	3220 (3)	321 (4)
C(3)	103 (3)	2435 (3)	4639 (3)	408 (6)
C(4)	-463 (3)	2341 (4)	5969 (3)	517 (7)
C(5)	-1408 (3)	1035 (4)	5940 (4)	547 (8)
C(6)	-1780 (3)	-188 (4)	4618 (3)	484 (7)
C(7)	-1614 (2)	-1438 (3)	1872 (3)	370 (5)
C(8)	1572 (3)	4940 (4)	5942 (4)	599 (7)
C(9)	2612 (4)	6067 (4)	5525 (5)	734 (9)
(IB)				
Ni	0	5000	0	279 (1)
O(1)	1507 (1)	4874 (2)	503 (2)	358 (3)
O(2)	3375 (2)	4310 (2)	1596 (3)	463 (4)
N	668 (2)	6752 (2)	-564 (2)	344 (4)
C(1)	2820 (2)	7319 (3)	442 (3)	383 (5)
C(2)	2596 (2)	5937 (2)	752 (3)	329 (4)
C(3)	3646 (2)	5688 (3)	1384 (3)	388 (5)
C(4)	4830 (3)	6778 (4)	1750 (4)	548 (7)
C(5)	5020 (3)	8173 (4)	1477 (6)	673 (10)
C(6)	4028 (2)	8412 (3)	802 (4)	543 (7)
C(7)	1810 (2)	7605 (3)	-290 (3)	376 (5)
C(8)	4337 (3)	4040 (4)	2487 (4)	520 (7)
C(9)	3727 (3)	2550 (5)	2784 (6)	776 (11)
(II)				
Ni	0	0	0	413 (1)
O(1)	-303 (3)	-705 (1)	1976 (4)	524 (6)
O(2)	-68 (3)	-1489 (2)	5446 (4)	585 (7)
N	-2045 (3)	-127 (2)	-1513 (5)	462 (8)
C(1)	-3013 (4)	-959 (2)	1085 (6)	473 (9)
C(2)	-1565 (4)	-1025 (2)	2398 (6)	442 (9)
C(3)	-1519 (4)	-1468 (2)	4272 (6)	484 (9)
C(4)	-2814 (4)	-1822 (2)	4820 (7)	574 (10)
C(5)	-4237 (5)	-1750 (2)	3486 (8)	644 (12)
C(6)	-4334 (4)	-1330 (2)	1699 (7)	585 (11)
C(7)	-3127 (4)	-529 (2)	-827 (6)	489 (9)
C(8)	131 (5)	-1899 (2)	7393 (7)	589 (10)
C(9)	1790 (5)	-1772 (3)	8363 (8)	694 (12)
C(10)	-2456 (4)	249 (2)	-3596 (6)	588 (11)
(III)				
Ni	0	0	0	390 (2)
O(1)	-118 (2)	652 (1)	1587 (5)	486 (5)
O(2)	-650 (3)	1430 (1)	4837 (5)	554 (6)
N	1748 (3)	205 (1)	-2004 (5)	414 (5)
C(1)	2266 (3)	1054 (1)	251 (7)	455 (7)
C(2)	929 (3)	1036 (1)	1749 (6)	435 (7)
C(3)	689 (4)	1468 (1)	3517 (6)	454 (7)
C(4)	1749 (4)	1879 (1)	3774 (7)	537 (8)
C(5)	3101 (4)	1888 (1)	2307 (8)	580 (9)
C(6)	3333 (4)	1485 (1)	543 (8)	562 (9)
C(7)	2522 (4)	647 (1)	-1649 (6)	456 (7)
C(8)	-955 (5)	1857 (1)	6578 (8)	576 (9)
C(9)	-2545 (0)	1734 (6)	7694 (2)	818 (13)
C(10)	2338 (4)	-140 (1)	-4077 (7)	462 (7)
C(11)	3671 (4)	-497 (2)	-2925 (9)	643 (10)

from a bend along a line joining the two donor atoms within each separate ligand. The molecular steps as measured by the perpendicular distances between planes of best fit through the two benzene rings are 0.144 and 0.696 Å in (I), 0.514 Å in (II) and 0.616 Å in (III). The stepping takes place entirely at the donor atoms since the deviations of the chelate-ring atoms O, N and C(7) from the benzene ring best planes amount to 0.026 (1) and 0.055 (1), 0.013 (1) and 0.026 (1), 0.043 (1) and 0.065 (2) Å in (I),

Table 3. Bond lengths (Å) and angles (°)

Primed atoms are related to unprimed atoms by a centre of symmetry.

	(I <sub>A</sub> )	(I <sub>B</sub> )	(II)	(III)
Ni—O(1)	1.836 (1)	1.846 (2)	1.815 (2)	1.833 (2)
Ni—N	1.850 (2)	1.851 (2)	1.917 (3)	1.921 (2)
O(1)—C(2)	1.315 (3)	1.305 (3)	1.291 (4)	1.307 (3)
N—C(7)	1.290 (3)	1.277 (3)	1.298 (4)	1.297 (4)
C(1)—C(7)	1.429 (3)	1.431 (3)	1.421 (5)	1.427 (5)
C(1)—C(2)	1.404 (4)	1.410 (3)	1.418 (5)	1.405 (4)
C(2)—C(3)	1.421 (3)	1.423 (3)	1.418 (5)	1.430 (4)
C(3)—C(4)	1.385 (4)	1.384 (4)	1.369 (5)	1.365 (5)
C(4)—C(5)	1.382 (5)	1.416 (5)	1.408 (5)	1.406 (5)
C(5)—C(6)	1.361 (5)	1.367 (4)	1.347 (6)	1.372 (5)
C(6)—C(1)	1.420 (3)	1.405 (4)	1.418 (5)	1.410 (4)
N—C(10)	—	—	1.476 (5)	1.472 (4)
C(10)—C(11)	—	—	—	1.510 (5)
C(3)—O(2)	1.372 (4)	1.366 (3)	1.376 (4)	1.358 (4)
O(2)—C(8)	1.423 (3)	1.429 (3)	1.420 (4)	1.431 (4)
C(8)—C(9)	1.488 (6)	1.507 (5)	1.507 (5)	1.495 (6)
O(1)—Ni—N	93.8 (1)	93.6 (1)	93.1 (1)	93.2 (1)
O(1)—Ni—N'	86.2 (1)	86.4 (1)	87.0 (1)	86.8 (1)
Ni—O(1)—C(2)	127.7 (1)	126.5 (1)	130.5 (2)	129.1 (2)
C(2)—C(1)—C(7)	120.6 (2)	119.8 (2)	120.0 (3)	120.4 (3)
C(1)—C(7)—N	124.5 (2)	125.2 (2)	127.3 (3)	127.3 (3)
C(7)—N—Ni	128.3 (2)	127.5 (2)	124.2 (3)	124.0 (2)
Ni—N—C(10)	—	—	119.5 (2)	121.8 (2)
C(7)—N—C(10)	—	—	116.3 (3)	114.2 (3)
N—C(10)—C(11)	—	—	—	111.8 (3)
C(1)—C(2)—C(3)	117.7 (2)	117.1 (2)	117.5 (3)	117.9 (3)
C(2)—C(3)—C(4)	120.7 (3)	121.4 (2)	122.0 (4)	120.7 (3)
C(3)—C(4)—C(5)	120.6 (3)	120.1 (3)	119.4 (4)	121.0 (3)
C(4)—C(5)—C(6)	120.5 (3)	119.4 (3)	120.5 (4)	119.3 (3)
C(5)—C(6)—C(1)	120.4 (3)	121.0 (3)	121.4 (4)	120.9 (3)
C(6)—C(1)—C(2)	120.1 (2)	120.9 (2)	119.2 (4)	120.1 (3)
C(2)—C(3)—O(2)	113.6 (2)	114.4 (2)	112.9 (3)	114.4 (3)
C(4)—C(3)—O(2)	125.5 (3)	124.2 (2)	125.1 (4)	124.9 (3)
C(3)—O(2)—C(8)	118.6 (2)	118.4 (2)	118.7 (3)	117.5 (3)
O(2)—C(8)—C(9)	107.3 (3)	106.4 (3)	106.1 (3)	107.5 (3)

0.001 (2), 0.055 (3) and 0.018 (3) Å in (II) and 0.010 (2), 0.056 (2) and 0.058 (2) Å in (III) respectively. Such changes in the conformation have been explained by steric (Tamura, Ogawa, Takeuchi & Yamada, 1979) and/or by electronic causes (Maslen & Waters, 1975). It is difficult to assess which of the factors are responsible or predominant for such behaviour, particularly keeping in mind the significant difference in the step heights within the two crystallographically independent molecules (*A*) and (*B*) in complex (I). However, it might be assumed that such a difference is also a consequence of the packing conditions between two molecules.

Further distinct features are the close intramolecular approaches between the O atoms O(1') ( $-x, -y, -z$ ) and the H atom H(1) bonded to N in (I) [2.361 (2) and 2.398 (2) Å], methyl H(101) and H(102) in (II) [2.457 (29) and 2.430 (40) Å] and methylene H(101) in (III) [2.162 (5) Å]. In (I) and particularly in (III) these distances are considerably shorter than the sum of the corresponding van der Waals radii (2.60 Å) (Pauling, 1963). It is most probable that these short contacts are important factors influencing the conformation of the complex molecules.

The Ni—O bond lengths are similar in (I) [1.836 (1) and 1.846 (2) Å] and (III) [1.833 (2) Å] but significantly shorter in (II) [1.815 (2) Å]. Those in (I)

and (III) are close to *e.g.* 1.827 (2) Å, the value found for such a bond in bis(*N*-ethylsalicylideneaminato)-nickel(II) (Jones *et al.*, 1985), 1.844 (7) Å in bis(*N*-allylsalicylideneaminato)nickel(II) (Bhatia *et al.*, 1981), 1.840 (4) Å in bis[*N*-(2,2-diethoxyethyl)salicylideneaminato]nickel (II) (Fernández-G. *et al.*, 1986) and 1.830 (2) Å in bis(5-chloro-*N*-ethylsalicylideneaminato)nickel(II). The Ni—O bond length of (II) is close to 1.818 (3) Å, the value found in bis(5-chloro-*N*-methylsalicylideneaminato)nickel(II) (Jones *et al.*, 1986). However, the Ni—N bond lengths in (II) [1.917 (3) Å] and (III) [1.921 (2) Å] are similar while those in (I) [1.850 (2) and 1.851 (2) Å] are considerably shorter and actually the shortest found in this class of compound (Bhatia *et al.*, 1981; Jones *et al.*, 1985; Britton & Pignolet, 1989).

The bond lengths within the benzene rings of all three structures show an interesting feature: three consecutive longer [C(6)—C(1), C(1)—C(2), C(2)—C(3)] and three relatively shorter bonds [C(3)—C(4), C(4)—C(5), C(5)—C(6)]. Such shortening and lengthening of the C—C bonds was also found in the previously mentioned chloro-derivative analogues as well as in some salicylideneaminato complexes of copper(II) (Maslen & Waters, 1975; Lingafelter & Braun, 1966). Furthermore, in all three structures two of the benzene ring bonds, C(3)—C(4) and C(5)—C(6), are distinctly shorter so as to suggest quinonoid character of the rings.

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## Structure of Bis(dimethylphenylphosphine)(*meso*-5,10,15,20-tetraphenylporphinato)-iron(III) Perchlorate

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**Abstract.** [Fe(C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>)(C<sub>8</sub>H<sub>11</sub>P)<sub>2</sub>]ClO<sub>4</sub>, *M<sub>r</sub>* = 985.4, monoclinic, *C2/c*, *a* = 25.127 (9), *b* = 15.174 (5), *c* = 15.239 (5) Å, β = 110.22 (3)°, *V* = 5452 (1) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.23 Mg m<sup>-3</sup>, λ(Mo *Kα*) = 0.71073 Å, μ = 4.04 cm<sup>-1</sup>, *F*(000) = 2112, *T* = 297 K. Final *R* = 0.060 for 2766 observed reflections. This first X-ray study of a phosphine–porphinato–iron(III) complex confirms the low-spin state of the ferric atom. The metal–phosphorus bond length [2.350 (1) Å] is longer than those observed in the analogous iron(II) complex containing dimethylphosphine ligands [2.284 (1) Å].

**Introduction.** This investigation is part of a program to examine the structure of phosphine–iron–porphyrin complexes (Sodano, Simonneaux & Toupet, 1988). Phosphines with small alkyl groups are new structural probes of hemoproteins (Bondon, Petrinko, Sodano & Simonneaux, 1986) and are a class of ligands which can bind to both valence states of hemoglobin (Fe<sup>II</sup> and Fe<sup>III</sup>) (Simonneaux, Bondon & Sodano, 1987). As an essential complement of our hemoprotein studies, it is of interest to understand the effect of the phosphine on the ferric porphyrin structure because of the absence of structural studies on model phosphine complexes of iron(III).

**Experimental.** The sample (prism 0.25 × 0.25 × 0.30 mm) was obtained by crystallization from a 50/50 mixture of dichloromethane and hexane. Data collection on an Enraf–Nonius CAD-4 diffractometer. Unit cell and standard deviations were obtained from a least-squares fit of 25 reflections, 8 < θ < 12°. Unique data set: *h* 0–28, *k* 0–17, *l* –17–17, 2θ<sub>max</sub> = 54°, scan ω/2θ = 1, Zr-filtered Mo *Kα* radiation; intensity control reflections without appreciable decay (226, 226, 12, 0, 2); 6397 reflections measured, 2766 unique (*R*<sub>int</sub> = 0.013) with *I* > 3.0σ(*I*). After data reduction (Lorentz and polarization correction, no absorption correction), resolution of the structure in centrosymmetric group *C2/c* by direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) revealed the porphinato moiety. The remaining phenyl groups, the dimethylphenylphosphine ligand and ClO<sub>4</sub><sup>-</sup> were found with Fourier techniques. The perchlorate anion appears disordered. The porphyrin structure was anisotropically refined and the H atoms placed in fixed positions respecting stereochemistry. The best full-matrix least-squares refinement (on *F*) of the structure {*x*, *y*, *z*, β<sub>*ij*</sub> for Fe, P, Cl, N and C atoms; *x*, *y*, *z*, *B* for O; 346 variables and 2766 observations; max. Δ/σ = 0.22; *w* = 1/σ(*F<sub>o</sub>*)<sup>2</sup> = [σ<sup>2</sup>(*I*) + (0.04*F<sub>o</sub>*<sup>2</sup>)<sup>2</sup>]<sup>-1/2</sup>} gives *R* =