Crystal Structure of Di-iodo[ethylenebis(oxyethylene)]bis(diphenylphosphine)nickel(II)

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The structure of the Ni(poop)I_2 complex {poop = [ethylenebis(oxyethylene)]bis(diphenylphosphine)} has been determined by X-ray analysis. The crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 11\cdot56 \pm 0\cdot01$, $b = 18\cdot32 \pm 0\cdot03$, $c = 14\cdot88 \pm 0\cdot03$ Å, and $\beta = 111\cdot5 \pm 0\cdot2°$. The structure has been solved by the heavy-atom technique and refined by full-matrix least-squares to R $0\cdot091$ over 1654 independent observed reflections, collected by photographic methods.

This is the first low-spin nickel(II) complex whose structure has been shown by X-ray to be an example of co-ordination intermediate between square planar and tetrahedral. The donor set is formed by two iodine and two phosphorus atoms. Statistically the oxygen atoms occupy two positions: in the position closer to the metal, the Ni $\cdots$ O distances are $3\cdot20(7)$ and $3\cdot16(6)$ Å. These contacts contribute to the stabilization of this unusual co-ordination.

RECENTLY the structure of the high-spin complex of nickel(II) chloride with oxydiethylenebis(diphenylphosphine), $Ph_2P\cdot[CH_2]_2\cdot O\cdot[CH_2]_2\cdot PPh_2$ (pop), was reported.[1] The co-ordination polyhedron about the nickel atom is a distorted tetrahedron with a P_2Cl_2 donor set, the oxygen atom being non-co-ordinated (Ni $\cdots$ O $3\cdot64$ Å). Another diphenyldiphosphine, with a longer chain containing two oxygen atoms, [ethylenebis(oxyethylene)]bis(diphenylphosphine) (poop), reacts with NiI_2, to give a monomeric complex Ni(poop)I_2,[2] which, in contrast to Ni(pop)Cl_2, is low-spin. The possible stereochemistries for this complex are therefore either five- or four-co-ordinate (square planar), depending on whether the ligand is bi- or ter-dentate. The electronic spectrum of this compound does not indicate unambiguously the co-ordination about the nickel atom, since it differs from reference spectra of square-planar and five-co-ordinate nickel(II) complexes. We have therefore undertaken an X-ray analysis of Ni(poop)I_2. The spectral properties of this compound and preliminary results of the crystal structure were briefly reported previously.[3]

EXPERIMENTAL

Crystal Data.—$C_{30}H_{32}I_2NiO_2P_2$, $M = 799\cdot05$, Monoclinic, $a = 11\cdot56 \pm 0\cdot01$, $b = 18\cdot32 \pm 0\cdot03$, $c = 14\cdot88 \pm 0\cdot03$ Å, $\beta = 111\cdot5 \pm 0\cdot2°$, $U = 2932\cdot7$ Å^3, $D_m = 1\cdot79$, $Z = 4$, $D_c = 1\cdot80$, $F(000) = 1568$. Space group $P2_1/c$. Cu-K_α radiation, $\lambda = 1\cdot5418$ Å, $\mu(Cu\text{-}K_\alpha) = 189$ cm.$^{-1}$.

Data Collection.—Crystals of Ni(poop)I_2 were prepared from the ligand and NiI_2 in n-butyl alcohol. Cell parameters were determined by a least-squares refinement of 30 values of 2θ from $h0l$ and $hk0$ Weissenberg photographs.

Several crystals were used for the collection of the intensities, owing to their decomposition. They were all plate-shape with dimensions *ca.* $0\cdot03 \times 0\cdot1 \times 0\cdot4$ mm. The longest dimension was chosen as the rotation axis and doubly integrated Weissenberg photographs of the layers $hk0$—9 were taken on a Nonius camera by the multiple-film equi-inclination technique with Cu-K_α radiation. The

intensities of a total of 1654 reflections were measured on a Nonius microdensitometer and corrected for Lorentz and polarization effects. The various levels were put on a common scale by means of two Weissenberg photographs, containing 30° samples from each level. The atomic scattering factors were taken from ref. 4. Corrections for anomalous scattering of nickel ($\Delta f' = -3\cdot1$ e) and iodine atoms ($\Delta f' = -1\cdot6$, $\Delta f'' = 7\cdot0$ e) were included.[5]

Structure Determination.—The positions of the two iodine atoms and of the nickel atom were obtained from a three-dimensional Patterson synthesis. Two three-dimensional Fourier syntheses showed the positions of all non-hydrogen atoms; R was then $0\cdot17$. These calculations were performed on an IBM 1620, with programmes written by Albano *et al.*[6] Refinement was continued on an IBM 7090 with the full-matrix least-squares programme of Busing and Levy, adapted for this computer by Stewart.[7] The weighting scheme used was $w = 1$ for $F_o \leqslant 100$ and $\sqrt{w} = 100/F_o$ for $F_o > 100$. A difference Fourier synthesis calculated in an intermediate stage of this refinement showed that each oxygen atom occupies statistically two positions differing in orientation about the C–C axis in the C–O–C moiety. Occupancy factors are close to 50% for the two positions as evidenced by the height of the difference Fourier peaks and by the subsequent refinement, which gave values in the range 45—55%. Temperature factors of O(1) and O(2) dropped from $9\cdot6$ and $10\cdot7$ Å^2, respectively, to $4\cdot8$ and $5\cdot2$ Å^2 [O(1) and O(1')] and $3\cdot8$ and $5\cdot5$ Å^2 [O(2) and O(2')] after disorder was considered. Individual isotropic temperature factors were used for the oxygen and carbon atoms, whereas heavier atoms were allowed to vibrate anisotropically. Several cycles of refinement on positional and thermal parameters and scale factors gave R $0\cdot091$ and the weighted value, R', $0\cdot115$, where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

No attempt was made to locate the hydrogen atoms, owing to the rather poor quality of the data. A final difference Fourier synthesis did not show any remarkable features, apart from some peaks of *ca.* $0\cdot5$ eÅ^{-3} attributable to hydrogen atoms.

The designation of the atoms is shown in Figure 1. The

1 P. T. Greene and L. Sacconi, *J. Chem. Soc. (A)*, 1970, 866.
2 L. Sacconi unpublished results.
3 L. Sacconi and P. Dapporto, *J. Amer. Chem. Soc.*, 1970, **92**, 4133.
4 D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

5 D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.
6 V. Albano, P. L. Bellon, and F. Pompa, *Ricerca sci. Suppl.*, 1963, **33**, 285; V. Albano, P. L. Bellon, F. Pompa, and V. Scatturin, *Ricerca sci. Suppl.*, 1963, **33**, 1067.
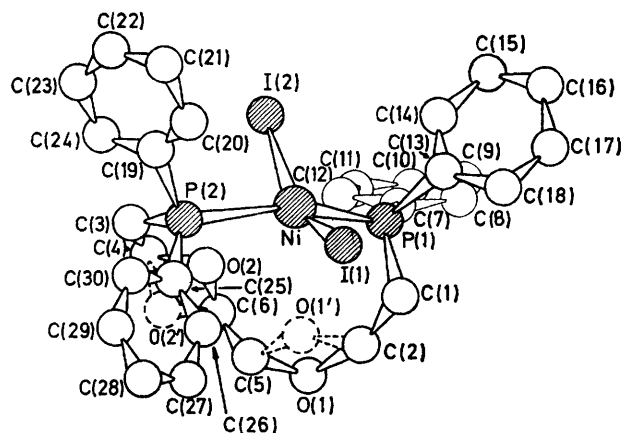7 J. M. Stewart, Technical Report TR 64–6, University of Maryland Computer Science Centre, 1964.

FIGURE 1   A perspective view of the molecule

final values of the parameters and their standard deviations are reported in Tables 1 and 2.†

TABLE 1

Final atomic co-ordinates ($\times 10^4$) and isotropic thermal parameters with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	B (Å^2)
I(1)	−404(2)	2058(1)	2119(2)	*
I(2)	−2995(2)	4000(1)	2345(2)	*
Ni	−1711(4)	3190(2)	1743(4)	*
P(1)	−3270(7)	2547(4)	690(8)	*
P(2)	−89(7)	3949(4)	2370(7)	*
O(1)	−2508(63)	3289(33)	−675(51)	4·8(1·4)
O(1′)	−1838(61)	3184(32)	−441(50)	5·2(1·4)
O(2)	−1937(55)	4535(29)	353(47)	3·8(1·2)
O(2′)	−979(56)	4605(31)	346(49)	5·5(1·2)
C(1)	−2870(42)	2116(24)	−198(38)	3·7(1·0)
C(2)	−2455(50)	2628(28)	−940(46)	6·1(1·2)
C(3)	−400(45)	4874(25)	1974(41)	4·5(1·0)
C(4)	−1074(45)	5002(27)	939(44)	4·9(1·1)
C(5)	−1848(39)	3830(22)	−1094(37)	4·2(1·0)
C(6)	−2131(58)	4537(31)	−669(52)	6·3(1·5)
C(7)	−4686(30)	2996(18)	32(29)	2·1(0·6)
C(8)	−5760(41)	2618(23)	−547(38)	3·4(1·0)
C(9)	−6885(35)	2907(21)	−1170(33)	3·5(0·8)
C(10)	−6893(44)	3704(25)	−1411(39)	5·1(1·1)
C(11)	−5737(36)	4081(21)	−762(33)	3·6(0·8)
C(12)	−4787(34)	3780(18)	−190(32)	2·7(0·7)
C(13)	−3810(31)	1784(17)	1158(30)	1·8(0·6)
C(14)	−3901(37)	1069(22)	850(34)	3·2(0·8)
C(15)	−4465(41)	533(23)	1266(37)	5·9(0·9)
C(16)	−4972(40)	734(23)	1865(36)	6·9(0·9)
C(17)	−5039(47)	1458(27)	2240(41)	5·2(1·1)
C(18)	−4512(39)	1958(22)	1742(36)	3·8(0·9)
C(19)	528(28)	4096(16)	3611(27)	1·3(0·6)
C(20)	601(48)	3456(27)	4214(46)	5·2(1·1)
C(21)	1007(41)	3535(23)	5123(42)	6·0(0·9)
C(22)	1615(46)	4212(26)	5777(41)	4·7(1·1)
C(23)	1449(48)	4825(28)	5060(48)	5·6(1·2)
C(24)	977(45)	4743(26)	4111(43)	4·8(1·1)
C(25)	1263(32)	3731(18)	2106(31)	2·3(0·7)
C(26)	1041(35)	3454(20)	1186(33)	2·5(0·8)
C(27)	2104(46)	3342(25)	956(39)	4·5(1·0)
C(28)	3203(44)	3527(25)	1497(41)	4·9(1·0)
C(29)	3445(53)	3786(28)	2441(48)	5·7(1·2)
C(30)	2388(36)	3886(21)	2666(33)	2·8(0·8)

* These atoms were refined anisotropically.

DISCUSSION

The structure consists of discrete molecules of Ni(poop)I$_2$ (Figure 1). The nickel atom is four-co-

ordinated, linked to the two phosphorus and the two iodine atoms. A view of the structure down the c axis is given in Figure 2. Tables 3 and 4 list intramolecular

TABLE 2

Anisotropic thermal parameters ($\times 10^4$) for the atoms refined anisotropically,* with estimated standard deviations in parentheses

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	61(2)	19(1)	49(2)	5(1)	21(1)	−1(1)
I(2)	63(2)	20(1)	33(2)	4(1)	29(1)	−3(1)
Ni	50(5)	13(1)	34(5)	4(2)	24(3)	−1(2)
P(1)	51(7)	15(2)	38(9)	3(3)	28(6)	1(3)
P(2)	49(7)	20(2)	16(8)	1(3)	19(5)	1(3)

* Thermal factors are in the form:

$$\exp(-\Sigma_{i=1}^3 \Sigma_{j=1}^3 h_i h_j \beta_{ij}).$$

distances and angles with their standard deviations. The co-ordination geometry can be described as intermediate between square planar and tetrahedral, as evidenced by the values of the angles about the nickel atom: I(1)–Ni–I(2) 143·5(0·3), I(1)–Ni–P(1) 89·2(0·3), I(1)–Ni–P(2) 94·3(0·3), I(2)–Ni–P(1) 97·6(0·3),
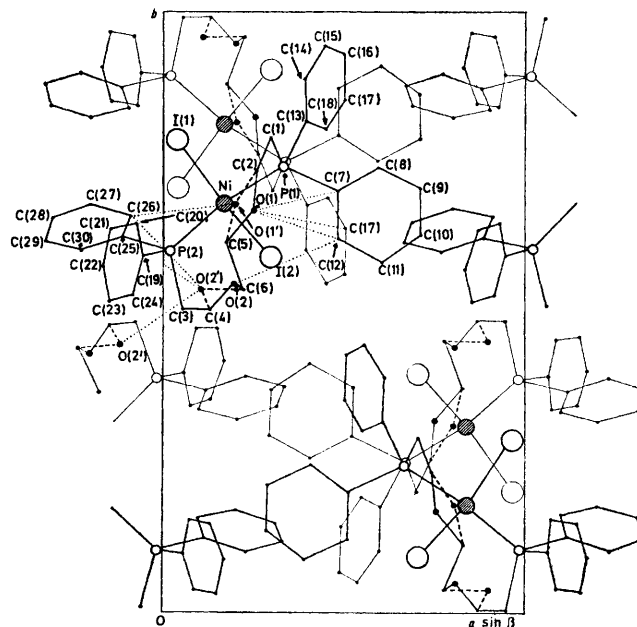
FIGURE 2   Schematic packing diagram of the structure as viewed down the c axis

I(2)–Ni–P(2) 90·0(0·3), and P(1)–Ni–P(2) 162·1(0·4)°. This distortion from planarity is again more evident if the displacements from the least-squares plane calculated by the positions of the nickel, the two iodine, and the two phosphorus atoms are considered. The deviations from the plane of equation $-4·17x - 7·25y + 13·90z = 1$ (monoclinic co-ordinates) are: Ni −0·17, I(1) +0·61, I(2) +0·60, P(1) −0·52, and P(2) −0·52 Å.

TABLE 3

Bond lengths and intramolecular distances (Å)

Ni–I(1)	2·505(6)	C(13)–C(18)	1·42(6)
Ni–I(2)	2·485(6)	C(14)–C(15)	1·44(6)
Ni–P(1)	2·242(11)	C(15)–C(16)	1·29(7)
Ni–P(2)	2·244(10)	C(16)–C(17)	1·45(7)
P(1)–C(1)	1·74(5)	C(17)–C(18)	1·44(7)
P(1)–C(7)	1·77(3)	C(19)–C(20)	1·46(6)
P(1)–C(13)	1·77(4)	C(19)–C(24)	1·39(6)
P(2)–C(3)	1·79(4)	C(20)–C(21)	1·27(9)
P(2)–C(19)	1·74(4)	C(21)–C(22)	1·57(7)
P(2)–C(25)	1·79(4)	C(22)–C(23)	1·51(8)
O(1)–C(2)	1·28(8)	C(23)–C(24)	1·32(9)
O(1)–C(5)	1·52(8)	C(25)–C(26)	1·39(6)
O(1')–C(2)	1·31(8)	C(25)–C(30)	1·29(5)
O(1')–C(5)	1·53(8)	C(26)–C(27)	1·41(6)
O(2)–C(4)	1·36(8)	C(27)–C(28)	1·28(7)
O(2)–C(6)	1·45(10)	C(28)–C(29)	1·41(9)
O(2')–C(4)	1·18(8)	C(29)–C(30)	1·39(7)
O(2')–C(6)	1·61(9)		
C(1)–C(2)	1·65(8)	Ni · · · O(1)	3·38(7)
C(3)–C(4)	1·47(8)	Ni · · · O(1')	3·20(7)
C(5)–C(6)	1·53(7)	Ni · · · O(2)	3·16(6)
C(7)–C(8)	1·41(6)	Ni · · · O(2')	3·61(6)
C(7)–C(12)	1·47(5)	O(1') · · · C(26)	3·36(8)
C(8)–C(9)	1·39(6)	O(1) · · · C(7)	3·11(8)
C(9)–C(10)	1·50(6)	O(1) · · · C(12)	3·11(8)
C(10)–C(11)	1·50(6)	O(2) · · · C(12)	3·39(7)
C(11)–C(12)	1·25(6)	O(2') · · · C(25)	3·34(7)
C(13)–C(14)	1·38(5)	O(2') · · · C(26)	3·05(7)

TABLE 4

Bond angles (deg.) with their estimated standard deviations

I(1)–Ni–I(2)	143·5(0·3)	P(1)–C(7)–C(12)	124·0(2·5)
I(1)–Ni–P(1)	89·2(0·3)	C(8)–C(7)–C(12)	111·3(3·3)
I(1)–Ni–P(2)	94·3(0·3)	C(7)–C(8)–C(9)	128·3(3·8)
I(2)–Ni–P(1)	97·6(0·3)	P(1)–C(7)–C(8)	122·7(2·8)
I(2)–Ni–P(2)	90·0(0·3)	C(8)–C(9)–C(10)	116·7(3·6)
P(1)–Ni–P(2)	162·1(0·4)	C(9)–C(10)–C(11)	111·5(3·8)
Ni–P(1)–C(1)	113·6(1·6)	C(10)–C(11)–C(12)	126·3(3·8)
Ni–P(1)–C(7)	119·1(1·2)	C(7)–C(12)–C(11)	124·3(3·5)
Ni–P(1)–C(13)	116·7(1·4)	P(1)–C(13)–C(14)	127·8(3·2)
C(1)–P(1)–C(7)	103·8(2·1)	P(1)–C(13)–C(18)	115·0(2·6)
C(1)–P(1)–C(13)	99·8(2·0)	C(14)–C(13)–C(18)	115·1(3·4)
C(7)–P(1)–C(13)	101·3(1·6)	C(13)–C(14)–C(15)	119·8(4·0)
Ni–P(2)–C(3)	114·4(1·6)	C(14)–C(15)–C(16)	119·7(4·0)
Ni–P(2)–C(19)	119·5(1·1)	C(15)–C(16)–C(17)	129·1(4·4)
Ni–P(2)–C(25)	115·8(1·2)	C(16)–C(17)–C(18)	106·9(4·3)
C(3)–P(2)–C(19)	99·0(2·1)	C(13)–C(18)–C(17)	127·6(3·8)
C(3)–P(2)–C(25)	103·1(2·0)	P(2)–C(19)–C(20)	115·9(3·0)
C(19)–P(2)–C(25)	102·5(1·7)	P(2)–C(19)–C(24)	128·8(3·2)
C(2)–O(1')–C(5)	111·5(5·6)	C(20)–C(19)–C(24)	115·3(4·2)
C(2)–O(1)–C(5)	113·8(5·7)	C(19)–C(20)–C(21)	118·7(4·4)
C(4)–O(2)–C(6)	117·8(5·3)	C(20)–C(21)–C(22)	131·1(4·6)
C(4)–O(2')–C(6)	118·5(5·5)	C(21)–C(22)–C(23)	103·7(4·4)
P(1)–C(1)–C(2)	118·3(3·3)	C(22)–C(23)–C(24)	124·4(4·7)
O(1')–C(2)–C(1)	107·1(5·3)	C(19)–C(24)–C(23)	126·4(4·7)
O(1)–C(2)–C(1)	105·8(5·2)	P(2)–C(25)–C(26)	115·8(2·7)
P(2)–C(3)–C(4)	117·5(3·6)	P(2)–C(25)–C(30)	124·2(3·3)
O(2)–C(4)–C(3)	123·8(4·9)	C(26)–C(25)–C(30)	119·6(3·6)
O(2')–C(4)–C(3)	121·8(5·2)	C(25)–C(26)–C(27)	115·4(3·7)
O(1')–C(5)–C(6)	110·1(4·7)	C(26)–C(27)–C(28)	124·4(5·0)
O(1)–C(5)–C(6)	99·6(4·4)	C(27)–C(28)–C(29)	120·4(5·0)
O(2)–C(6)–C(5)	117·3(4·9)	C(28)–C(29)–C(30)	114·4(4·8)
O(2')–C(6)–C(5)	103·0(4·4)	C(25)–C(30)–C(29)	125·4(4·6)

Previous X-ray structural determinations have shown all low-spin four-co-ordinate nickel(II) complexes to be either perfectly planar or very slightly distorted, with the greatest tetrahedral distortion being 173°, as found in the biacetylbis(mercaptoethylimine)nickel(II) complex.[8] The complex Ni(poop)I₂, therefore, has the

[8] Q. Fernando and P. J. Wheatley, *Inorg. Chem.*, 1965, **4**, 1726.

[9] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, Conformational Analysis,' Interscience, New York, 1965, p. 6.

largest distortion toward a tetrahedron so far found by X-ray analysis for a low-spin four-co-ordinate nickel(II) complex.

The oxygen atoms are at the short contact distances of 3·20(7) and 3·16(6) Å from the nickel atom in the closer contact positions, whereas in the other positions the distances are 3·38(7) and 3·61(6) Å. Considering the four possible geometries of the chain, it is apparent that the two having an oxygen close and the other oxygen distant from the metal atom are stabilized, since in these cases the geometry of the O·CH₂·CH₂·O chain is nearer to the 'staggered' configuration (Figure 3), which has been found to be the most stable in ethylenic chains.[9]
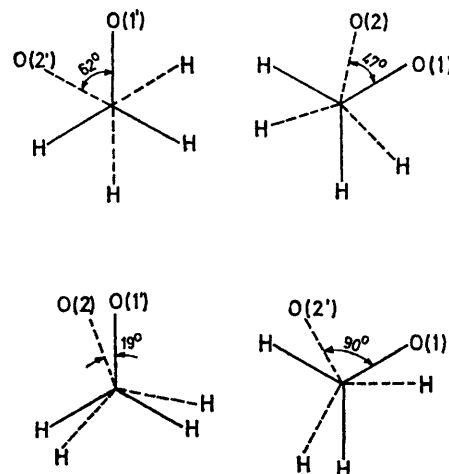

FIGURE 3 View along the C–C axis of the four possible arrangements of the O–CH₂–CH₂–O moiety of the chain of the ligand. O(1') and O(2) are in their positions closest to the metal. The hydrogen atoms are in calculated positions

If two methylene groups are substituted for the two oxygen atoms of poop, the resulting ligand gives with NiI₂ a high-spin complex of formula {Ph₂P·[CH₂]₈·PPh₂}NiI₂.[3] The electronic spectrum of this complex is characteristic of a tetrahedral geometry. Since the chain between the two phosphorus atoms in the poop ligand has nearly the same length as the [CH₂]₈ chain (taking C–C 1·54, C–O 1·43 Å),[10] the unusual co-ordination geometry about the nickel atom found in the Ni(poop)I₂ complex seems to be stabilized by the Ni · · · O interaction. This interaction prevents the formation of a tetrahedral complex by opening the P(1)–Ni–P(2) angle (162·1°). If the other angle between the ligands opposite to the nickel is considered, e.g. the I(1)–Ni–I(2) angle (143·5°), it is, in fact, found to be closer to the expected value for tetrahedral geometry. This closeness is evident if the value is compared not with the theoretical value of 109° 28', but with those found in distorted tetrahedral (Ph₃P)₂NiX₂ complexes, e.g. Cl–Ni–Cl 123° (ref. 11) and Br–Ni–Br 126° (ref. 12),

[10] *Chem. Soc. Special Publ.*, No. 18, 1965.

[11] G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 1963, 3625.

[12] J. A. J. Jarvis, R. H. B. Mais, and P. G. Owston, *J. Chem. Soc.* (*A*), 1968, 1473.

taking into account, furthermore, that a greater value for a I–Ni–I angle would be expected.

The Ni–P distances [2·242(11) and 2·244(10) Å] are in the range found in other square planar nickel(II) complexes, *e.g.* 2·26 in $(Et_3P)_2NiBr_2$ (ref. 13) and 2·263 Å in $Ni[P(CH_2Ph)Ph_2]Br_2$.[14] Also the Ni–I distances [2·505(6) and 2·485(6) Å] have the expected values, when they are compared with the Ni–I distance found in $[Ni(nop_2)I]I$ (2·474 Å),[15] [(nop_2) is *NN*-bis-(2-diphenyl-phosphinoethyl)-2-methoxyethylamine] which is described as a square pyramidal complex with an unusually long apical distance (Ni–O 2·62 Å). Distances and angles in the rest of the molecule do not differ by more than 3σ from the expected values, except for the angle C(21)–C(22)–C(23) in one phenyl group, which differs by *ca.* 4σ. The standard deviations for distances and angles are rather high: this is probably due to the decomposition of the crystals during data collection.

The oxygen atoms of the chain form very short intra-

and inter-molecular contacts, especially with carbon atoms of the phenyl groups, in addition to the contacts with the nickel atom mentioned earlier (Tables 3 and 5).

TABLE 5

Intermolecular distances $<3·5$ Å

O(2′) · · · O(2′ᴵ)	3·16	C(10) · · · C(17ᴵᴵᴵ)	3·44
C(23) · · · C(23ᴵᴵ)	3·35	C(11) · · · C(17ᴵᴵᴵ)	3·49
O(1) · · · C(17ᴵᴵᴵ)	3·43	C(2) · · · C(18ᴵᴵᴵ)	3·48

Roman numerals as superscripts refer to atoms in the following equivalent position relative to the reference molecule at x, y, z:

I $-x, 1-y, -z$ III $x, \frac{1}{2}-y, z-\frac{1}{2}$
II $-x, 1-y, 1-z$

The oxygen atoms, therefore, have a remarkable influence on the configuration of the molecule and on the structural packing. In Figure 2 the shortest contacts concerning the oxygen atoms are illustrated.

[13] G. Giacometti, V. Scatturin, and A. Turco, *Gazzetta*, 1958, **88**, 434.

[14] B. T. Kilbourn and H. M. Powell, *J. Chem. Soc. (A)*, 1970, 1688.

[15] P. Dapporto, R. Morassi, and L. Sacconi, *J. Chem. Soc. (A)*, 1970, 1298.