Diverse Donor Properties exhibited by the Facultative Diphosphine Diether Ligand, 1,8-Bis(diphenylphosphino)-3,6-dioxaoctane: Six- and Four-co-ordinate Complexes and *trans* Bidentate Behaviour

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Reaction of the title ligand (dpdo) with nickel(II) salts leads to the isolation of [Ni(dpdo)X_2] (X = Cl, Br, I, or NCS) complexes. In the solid state the previously prepared complex [Ni(dpdo)I_2] is distorted square planar, whilst [Ni(dpdo)X_2] (X = Cl or Br) are pseudo-tetrahedral; all are planar in methylene chloride. A single-crystal *X*-ray analysis of the thiocyanate complex shows a monomeric planar species possessing a P–M–P angle of 175.9°. The ligand co-ordinates as a *trans*-bidentate diphosphine. The subtle effects governing the co-ordination properties of this ligand are illustrated by the isolation of the blue planar [Ni(dpdo)Br_2]·C_6H_5Me complex. The pseudo-octahedral complex [Ni(dpdo)Cl_2]·$4H_2O$ and the planar [Ni(dpdo)$(H_2O)_2$][BF_4]$_2$ have also been isolated.

THERE is renewed interest in the nature of the chelate effect.[1] This is in part due to the studies of Venanzi and co-workers [2,3] on ligands such as 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene [2] which form *trans* square-planar complexes of the type [MX(CO)L] and [M(CO)(CH_3CN)L]BF_4 (M = Rh or Ir; X = Cl, Br, I, or NCS), and to those of Shaw and co-workers [4–6] who have prepared large ring (12—45 membered) complexes of the type *trans*-[{$MCl_2[Bu^t_2P(CH_2)_nPBu^t_2]$}$_x$] (M = Pd or Pt; *n* = 8, 9, 10, or 12; *x* = 1, 2, or 3) by treating [$MCl_2(PhCN)_2$] with the flexible long-chain diphosphines. Shaw has proposed that the presence of bulky groups attached to the donor atoms results in repulsive interactions between substituents in a *cis* geometry, hence favouring the formation of the *trans* complex, an argument in keeping with Shaw and co-workers' inability to synthesize *trans*-bonding diphosphine complexes which did not possess bulky groups. However, recent work by Hill *et al.*[7] on the donor properties of some α,ω-bis(diphenylphosphino)alkanes strongly suggests that the structures of the resulting palladium(II) complexes, including a large number of *trans* chelates, is a function of the length of the alkane chain. This is in agreement with earlier observations of McAuliffe and co-workers [8,9] that ligands with methyl or phenyl substituents are capable of *trans* chelation provided the backbone length is correct. These workers have even prepared *trans*-[$MLCl_2$] (M = Pd or Pt) and *trans*-[$PdLBr_2$] with L = 1,12-bis(phenylthio)dodecane.[10]

The stoicheiometric and structural effects of chelate chains of even short lengths are well established.[11] Sacconi and Dapporto [12] pioneered the development of ligands containing weak ether donors in addition to phosphine groups, *e.g.* the ligand 1,8-bis(diphenylphosphino)-3,6-dioxaoctane, $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$ (dpdo), which reacts with nickel(II) iodide to form [Ni(dpdo)I_2]. These authors have also obtained an *X*-ray crystal structure of this complex and describe it as a distorted tetrahedral molecule.[12] In fact, a better description of this diamagnetic compound would be a distorted *trans*-planar molecule, P–Ni–P 162.1°; there is no evidence for Ni–O bonding. In this respect dpdo acts very much as does the potentially quadridentate $Me_2As(CH_2)_2S(CH_2)_3S(CH_2)_3AsMe_2$ when it co-ordinates as a *trans*-diarsine ligand in the *trans*-planar [MLX_2] (M = Pd or Pt; X = Cl, Br, or I) species.[9,13] However, Alcock *et al.*[14,15] find that the ligands $Ph_2P(CH_2)_2(OCH_2CH_2)_nPPh_2$ (*n* = 1, 2, or 3) form complexes [Rh(CO)L]PF_6 in which the ligand is bidentate for *n* = 2 or 3 but tridentate for *n* = 1.

We are currently investigating the phenomenon of *trans* chelation,[7,10,13] and, in addition to synthesizing bidentate ligands with varying alkane chain lengths, we are examining facultative potentially quadridentate ligands which can act both as *trans*-chelating bidentate ligands or as ligands of higher denticity. That these quadridentate ligands are able to dissociate two M–L bonds to form *trans*-bidentate species is, in our opinion, an indication of the stability of *trans*-bidentate entities. We continue this approach by reporting our initial studies with the diphosphine diether dpdo first prepared by Sacconi and Dapporto.[12]

RESULTS AND DISCUSSION

The ligand 1,8-bis(diphenylphosphino)-3,6-dioxaoctane, dpdo, was prepared by the reaction of sodium diphenylphosphide with 1,8-dibromo-3,6-dioxaoctane in a 2 : 1 molar ratio under dinitrogen at 0 °C, according to equation (1). Crystallization from either hexane or ethanol gave the white solid ligand, m.p. 56 °C. The ^1H n.m.r. spectrum of dpdo (see Experimental section) can be divided into three distinct regions: (*i*) aromatic protons appear as a complex multiplet at 7.30 p.p.m. downfield from the internal $SiMe_4$ references (relative intensity 20); (*ii*) the aliphatic protons adjacent to the

$$2NaPPh_2 + Br(CH_2)_2O(CH_2)_2O(CH_2)_2Br \xrightarrow{Bu^n_2O} Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2 + 2NaBr \quad (1)$$

ether oxygens occur as a multiplet centred at 3.40 p.p.m. (relative intensity 8); and (*iii*) the aliphatic protons adjacent to the phosphorus atoms (H_a,H_b) occur as a triplet centred at 2.20 p.p.m. (relative intensity 4). The coupling constant $J(H_a-H_b)$ is 15 Hz, but no P-H coupling is observed.

TABLE 1

Elemental analysis, molecular-weight, conductivity, and magnetic-moment data for the complexes

Complex	Colour	Analysis (%) [a] C	H	X	Ni	M [b]	Λ [c] S/cm² mol⁻¹	$\mu_{eff.}$ (μ_B)
$[Ni(dpdo)Cl_2]$	Purple	58.2(58.5)	5.2(5.2)	11.3(11.5)	9.2(9.5)	543 (616)		3.25
$[Ni(dpdo)Br_2]$	Green	51.7(51.1)	4.8(4.5)	19.8(22.7)	8.4(8.3)	689 (705)		2.58
$[Ni(dpdo)I_2]$	Mustard	44.8(45.1)	4.0(4.0)	28.1(31.8)	7.9(7.4)			*d*
$[Ni(dpdo)(NCS)_2]$	Red	58.4(58.1)	5.0(4.8)	4.4(4.2) [e]	8.8(8.9)	634 (661)		*d*
$[Ni(dpdo)Br_2]\cdot C_6H_5CH_3$	Blue	56.2(55.7)	5.2(5.1)	20.7(20.1)	7.2(7.4)			2.00
$[Ni(dpdo)Cl_2]\cdot 4H_2O$	Turquoise	52.5(52.3)	5.1(5.8)	10.6(10.3)	8.6(8.5)			3.29
$[Ni(dpdo)(H_2O)_2][BF_4]_2$	Orange	48.3(47.7)	4.7(4.8)		7.6(7.8)	230 (754)	8.0 185.5 [f]	*d*

[a] Calculated values are given in parentheses. [b] Determined in chloroform. [c] 0.001 mol dm⁻³ solution in methylene chloride. [d] Diamagnetic. [e] X = N. [f] 0.001 mol dm⁻³ solution in nitromethane.

The ^{31}P n.m.r. spectrum of dpdo in deuteriochloroform with 85% phosphoric acid as an external standard exhibits a single peak at +21.8 p.p.m. upfield from the phosphoric acid peak. The ^{13}C spectrum, run in deuteriochloroform with $SiMe_4$ as an internal standard, was proton decoupled but did not exhibit P–C coupling. The *ipso-*, *ortho-*, *meta-*, and *para*-carbon atoms of the phenyls could all be distinguished, with P–C coupling being observed only for the *ipso-* and *ortho*-carbons [^1J(P–C) = 13.6, ^2J(P–C) = 19.1 Hz]. The larger value for ^2J(P–C) over ^1J(P–C) is typical. The aliphatic region showed resonances consistent with three distinct carbon nuclei: C^1, attached to the phosphorus and not to the more electronegative oxygen, has the highest up-field resonance, and ^1J(P–C) = 13.9 Hz. For C^2, ^2J(P–C) = 24.6 Hz.

The $[Ni(dpdo)X_2]$ (X = Cl, Br, I, or NCS) compounds were readily isolated from a 1 : 1 molar reaction of NiX_2 and dpdo in absolute ethanol. The solvated complexes were isolated as described in the Experimental section and Table 1.

The $[Ni(dpdo)X_2]$ (X = Cl or Br) complexes exhibit electronic solid-state reflectance spectra typical of pseudo-tetrahedral species,[16,17] Table 2 and Figure 1. The i.r. spectra (Table 3) are similarly in good agreement with this structure; the bands assignable to ν(M–X) in $[Ni(dpdo)Cl_2]$ (301, 336 cm⁻¹) and $[Ni(dpdo)Br_2]$ (225, 263 cm⁻¹) mirror those found for the pseudo-tetrahedral molecules $[Ni(PPh_3)_2Cl_2]$ (305, 341 cm⁻¹)[18] and $[Ni(PPh_3)_2Br_2]$ (232, 265 cm⁻¹).[19] The i.r. spectra are also useful in examining the denticity of the ligand. The antisymmetric ν(COC) bands for free dpdo occur as two

TABLE 2

Data from the reflectance and solution electronic spectra of the complexes

Complex	Reflectance $10^{-3}\lambda_{max.}$/cm⁻¹	Absorbance	Solution * $10^{-3}\lambda_{max.}$/cm⁻¹	ε/dm³ mol⁻¹ cm⁻¹
$[Ni(dpdo)Cl_2]$	26.1	1.30	32.4	sh
	19.2	1.16	26.7	6 890
	11.6	0.43	18.1	235
	9.7	sh		
	5.9	0.10		
$[Ni(dpdo)Br_2]$	26.6	0.75	36.8	9 570
	18.3	0.48	24.9	2 360
	11.6	0.40	16.6	254
	9.9	sh		
$[Ni(dpdo)I_2]$	25.8	0.62	43.9	12 170
	13.6	0.63	29.4	sh
			25.8	sh
			22.0	2 060
			14.9	363
$[Ni(dpdo)(NCS)_2]$	22.6—31.0 (br)	0.75	33.3	12 670
			26.2	9 370
$[Ni(dpdo)Br_2]\cdot C_6H_5CH_3$	26.2	0.45	40.5	10 530
	18.3	0.55	25.5	4 050
			17.0	
$[Ni(dpdo)Cl_2]\cdot 4H_2O$	30.4	0.55	32.4	sh
	16.7	0.47	26.7	7 170
	9.2	0.45	18.1	185
$[Ni(dpdo)(H_2O)_2][BF_4]_2$	33.3	0.70	31.2	9 680
	22.0	0.63	21.7	450

* In methylene chloride.

TABLE 3

Infrared data (cm^{-1}) for the complexes

Complex	ν(P–C)(aryl) [a]	ν(COC)	ν(Ni–X)	ν(Ni–X) [b]	ν(Ni–P)
dpdo	1 100s	1 110 (sh) 1 063s			
$[Ni(dpdo)Cl_2]$	1 100s	1 107s 1 070w (sh)	301m 336m	[c] 340 (sh)	225w 250w
$[Ni(dpdo)Br_2]$	1 100s	1 100s 1 070w (sh)	225m 263m		195w
$[Ni(dpdo)I_2]$	1 092m	1 110w (sh) 1 070w (sh)			
$[Ni(dpdo)(NCS)_2]$ [d]	1 100m	1 115m 1 066m			300w
$[Ni(dpdo)Br_2]\cdot C_6H_5CH_3$	1 098 (sh)	1 105m 1 060w	225w 250w		208w
$[Ni(dpdo)Cl_2]\cdot 4H_2O$ [e]	1 100s	1 070s		340 (sh)	
[f]		1 057s			

[a] Tentative assignment. [b] Solution spectrum in methylene chloride. [c] Hidden absorption. [d] This complex exhibited ν(CN) stretching absorptions at 2 090s cm^{-1} in the solid state and at 2 092 cm^{-1} in methylene chloride solution. [e] Band at 250s cm^{-1} in chloroform solution tentatively assigned to ν(Ni–O). [f] The complex $[Ni(dpdo)(H_2O)_2][BF_4]_2$ exhibited a strong broad band at 1 060 cm^{-1} characteristic of free BF_4^- ions.

strong absorptions at 1 063 cm^{-1} for the *gauche* configuration and 1 110 cm^{-1} for the *trans* configuration. It is invariably found that a shift to lower energy occurs for the ν(COC) when an alkyl ether is co-ordinated to a metal.[20,21] No shift is observed for ν(COC) of dpdo on co-ordination of NiX_2 (X = Cl or Br).

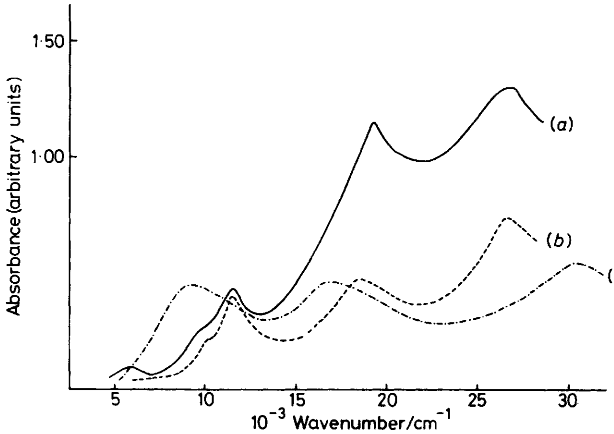


FIGURE 1 Reflectance spectra of the complexes $[Ni(dpdo)X_2]$, X = Cl (*a*) or Br (*b*), and $[Ni(dpdo)Cl_2]\cdot H_2O$ (*c*)

The room-temperature magnetic moments for $[Ni(dpdo)X_2]$ (X = Cl, Br, or I) form an interesting series, *viz.* 3.25 (Cl), 2.58 (Br), 0.0 (I) μ_B. This perhaps reflects the change in solid-state structure from pseudo-tetrahedral (Cl) to square planar (I), while the bromo-complex may well represent a spin-crossover point. Van Hecke and Horrocks[22] have similarly observed reduced magnetic moments (2.12—2.73 μ_B) for NiP_2X_2 species bordering on a planar $\rightleftharpoons$ tetrahedral crossover point.

The solution electronic spectra of $[Ni(dpdo)X_2]$ (X = Cl or Br), Figure 2, in methylene chloride are quite different from the reflectance spectra, Figure 1, and indicate a change in structure from pseudo-tetrahedral to square planar upon dissolution. For example, the spectrum of $[Ni(dpdo)Cl_2]$ in CH_2Cl_2 is quite similar to other square-planar NiP_2Cl_2 complexes,[16] and band assignments can be made *viz.* ${}^1A_{2g}\leftarrow{}^1A_{1g}$ (18 100 cm^{-1}) and ${}^1B_{1g}\leftarrow{}^1A_{1g}$ (26 700 cm^{-1}). It is most important to note that the $[Ni(dpdo)X_2]$ (X = Cl, Br, or NCS) complexes are monomeric in chloroform, Table 1. Taking into account the fact that *X*-ray crystallographic studies for $[Ni(dpdo)X_2]$ (X = I;[12] X = NCS, see below) show these complexes to be monomeric, it is with some confidence that we postulate the structures of $[Ni(dpdo)X_2]$ (X = Cl or Br) (see below).

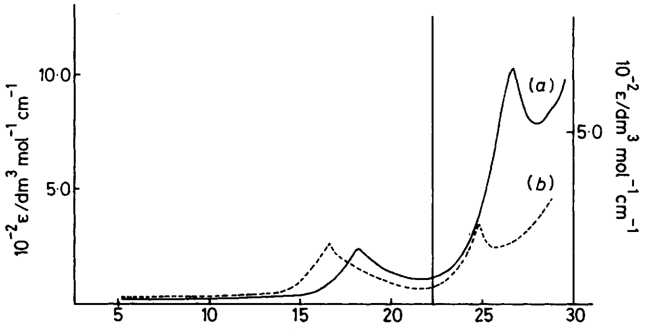
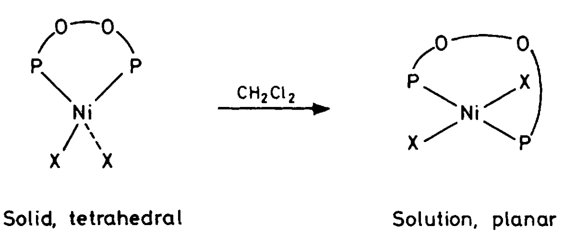


FIGURE 2 Solution spectra of the complexes $[Ni(dpdo)X_2]$, X = Cl (*a*) or Br (*b*)



The i.r. spectrum of the red diamagnetic complex $[Ni(dpdo)(NCS)_2]$ shows a single symmetrical absorption at 2 090 cm^{-1} in the solid state and at 2 092 cm^{-1} in methylene chloride solution (integrated intensity, A = 9.39 × 10^4 dm^3 mol^{-1} cm^2, $\Delta\nu_{\frac{1}{2}}$ = 26 cm^{-1})[23] indicating Ni–NCS linkages. The electronic reflectance spectrum and the spectrum of the complex in CH_2Cl_2 both indicate planar geometry (Figures 3 and 4). The latter exhibits intense bands at 26 200 ($\varepsilon = 9\,370$) and 33 300 cm^{-1} ($\varepsilon = 12\,670$ dm^3 mol^{-1} cm^{-1}). The former band has been tentatively assigned to the ${}^1B_{1g}\leftarrow{}^1A_{1g}$, ν_3, transition, since it is too intense to be the ν_2 transition (which usually has ε in the range 50—500 dm^3 mol^{-1} cm^{-1}). The ν_2 transition is probably masked by the more intense ν_3 transition.

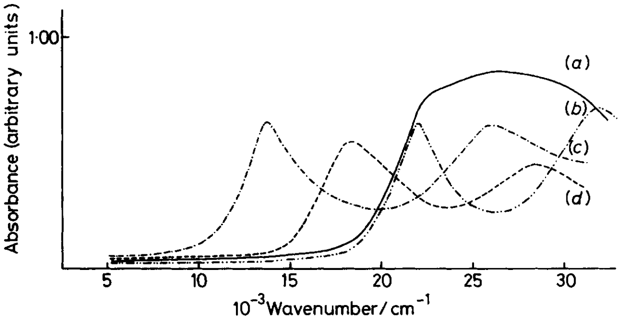


FIGURE 3 Reflectance spectra of the complexes [Ni(dpdo)(NCS)$_2$] (*a*), [Ni(dpdo)(H$_2$O)$_2$][BF$_4$]$_2$ (*b*), [Ni(dpdo)I$_2$] (*c*), and [Ni(dpdo)-Br$_2$]·C$_6$H$_5$Me (*d*)

A single-crystal *X*-ray diffraction study of [Ni(dpdo)(NCS)$_2$] was carried out to establish the precise nature of the metal co-ordination and the conformation of the macrocyclic ring. The results of the study are summarized in Figure 5 and Tables 4 and 5. As is the case for all [NiL$_2$(NCS)$_2$] complexes,[24] the nickel atom displays a *trans*-square-planar co-ordination, albeit with significant distortions, and the effectively linear thiocyanate anions are attached to the metal through the nitrogen-donor atom. The eleven-membered *trans*-bonded chelate ring is completed by the co-ordination of the phosphorus donor atoms of the diphosphine to nickel. Within the macrocycle, torsion angles involving non-hydrogen atoms about P–C and C–C bonds are close to ±60° and those about O–C bonds are within 10° of 180°. The sequences C(3)–C(4)–O(1)–C(5)–C(6) and C(5)–C(6)–O(2)–C(7)–C(8) thus define roughly planar staggered zigzags, the two planes being inclined at 60° to one another. The complex as a whole possesses approximate C_2 symmetry, the non-crystallographic diad axis passing through Ni and the midpoint of the C(5)–C(6) bond.

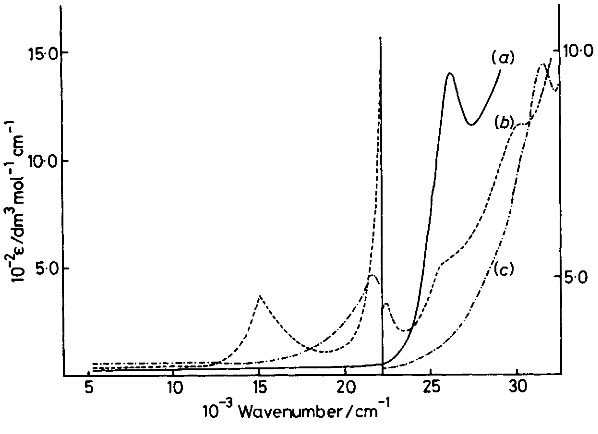


FIGURE 4 Solution spectra of the complexes [Ni(dpdo)X$_2$], X = NCS (*a*) or I (*b*), and [Ni(dpdo)(H$_2$O)$_2$][BF$_4$]$_2$ (*c*)

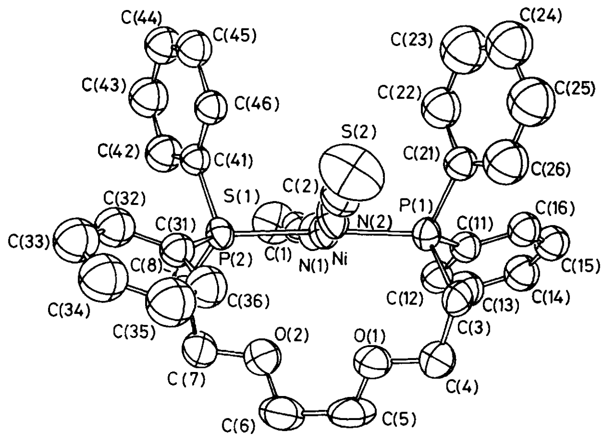


FIGURE 5 Perspective view of the molecule showing the atom-numbering scheme. 50% Probability ellipsoids are displayed

TABLE 4

Bond lengths (Å) in [Ni(dpdo)(NCS)$_2$]

Ni–P(1)	2.240(3)	P(2)–C(31)	1.813(6)
Ni–P(2)	2.233(3)	P(2)–C(41)	1.796(5)
Ni–N(1)	1.839(8)	O(1)–C(4)	1.384(13)
Ni–N(2)	1.828(8)	O(1)–C(5)	1.394(12)
S(1)–C(1)	1.608(10)	O(2)–C(6)	1.371(14)
S(2)–C(2)	1.591(10)	O(2)–C(7)	1.393(14)
P(1)–C(3)	1.858(10)	N(1)–C(1)	1.156(13)
P(1)–C(11)	1.814(5)	N(2)–C(2)	1.156(12)
P(1)–C(21)	1.802(6)	C(3)–C(4)	1.501(15)
P(2)–C(8)	1.824(9)	C(5)–C(6)	1.513(19)
		C(7)–C(8)	1.514(16)

TABLE 5

Selected angles (°) in [Ni(dpdo)(NCS)$_2$]

(*a*) Bond angles

P(1)–Ni–P(2)	175.9(1)	Ni–P(1)–C(3)	109.9(3)
P(1)–Ni–N(1)	97.4(2)	Ni–P(1)–C(11)	122.3(2)
P(1)–Ni–N(2)	84.4(2)	Ni–P(1)–C(21)	110.9(2)
P(2)–Ni–N(1)	85.9(2)	Ni–P(2)–C(8)	115.9(3)
P(2)–Ni–N(2)	92.8(2)	Ni–P(2)–C(31)	119.2(2)
N(1)–Ni–N(2)	169.9(4)	Ni–P(2)–C(41)	107.3(2)
Ni–N(1)–C(1)	166.6(7)	C(4)–O(1)–C(5)	112.7(9)
Ni–N(2)–C(2)	171.1(9)	C(6)–O(2)–C(7)	114.5(10)
N(1)–C(1)–S(1)	178.8(9)	P(1)–C(3)–C(4)	111.2(7)
N(2)–C(2)–S(2)	178.0(10)	P(2)–C(8)–C(7)	109.9(7)
C–P–C	102.0(4)—105.9(3), mean = 104.3(7)		
O–C–C	107.6(11)—109.8(9), mean = 108.6(5)		

(*b*) Torsion angles

Ni–P(1)–C(3)–C(4)	66(1)
P(1)–C(3)–C(4)–O(1)	−60(1)
C(3)–C(4)–O(1)–C(5)	172(1)
C(4)–O(1)–C(5)–C(6)	175(1)
O(1)–C(5)–C(6)–O(2)	56(1)
N(2)–Ni–P(2)–C(31)	−22(1)
Ni–P(2)–C(8)–C(7)	66(1)
P(2)–C(8)–C(7)–O(2)	−59(1)
C(8)–C(7)–O(2)–C(6)	170(1)
C(7)–O(2)–C(6)–C(5)	−175(1)
N(1)–Ni–P(1)–C(11)	−10(1)

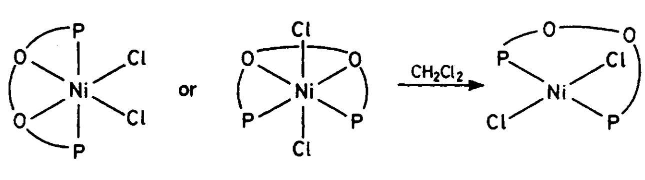
Bond lengths in [Ni(dpdo)(NCS)$_2$] are unexceptional, agreeing well with corresponding values in *trans*-[Ni(PPh$_2$Me)$_2$(NCS)$_2$] [25] and with the less accurately established values in [Ni(dpdo)I$_2$].[12] The structures of the three complexes, and in particular the nickel co-ordination polyhedra, show interesting differences which are best explained by variations in the severity of intramolecular overcrowding. In *trans*-[Ni(PPh$_2$Me)$_2$(NCS)$_2$] the most important interligand contacts are the N ··· C (methyl) separation of 3.17 Å and a N ··· C (phenyl) distance of 3.09 Å. The molecule is centrosymmetric, the nickel co-ordination is very nearly ideally square planar, and the Ni–N–C angles are close to linear [176.1(5)°]. In the electronically similar but conformationally more rigid species [Ni(dpdo)(NCS)$_2$] comparable N ··· C contacts are found [the shortest are N(1) ··· C(12) 3.15, N(2) ··· C(36) 3.05 Å]. However, this appears to be achieved at the expense of bending the thiocyanate ligands away from the phenyl groups with which they interact [N–Ni–N 169.9(4), Ni–N–C 166.6(7) and 171.1(9)°]. Opening of the P(1)–Ni–N(1) and P(2)–Ni–(2) angles [respectively 97.4(2) and 92.8(2)°] and of the Ni–P(1)–C(11) and Ni–P(2)–C(31) angles [respectively 122.3(2) and 119.2(2)°] may also help to relieve the N ··· C contacts. Interestingly, the P–Ni–P angle remains close to linear [175.9(1)°]. Replacement of NCS$^-$ by the more sterically demanding I$^-$ leads to a much more drastic distortion of the nickel co-ordination: in [Ni(dpdo)I$_2$] the P–Ni–P and I–Ni–I angles are 162.1(4) and 143.5(3)° respectively. The shortest I ··· C (phenyl) interligand separations are 3.60 Å, *ca.* 0.3 Å less than the sum of the van der Waals radii. The macrocyclic conformation in [Ni(dpdo)I$_2$] is obscured by disorder of the oxygen atoms. However, the torsion angles suggest that neither of the two more likely conformations is as energetically favourable as that found in [Ni(dpdo)(NCS)$_2$]. The contacts and torsion angles in [Ni(dpdo)I$_2$] were recalculated from ref. 12. The total range shown by P–C–C–O torsion angles is 1—36°. The I ··· C (α-methylene) interligand contacts of 3.58—3.62 Å may indicate that overcrowding influences the macrocycle conformation.

It is also worth noting that the Ni ··· O contacts in [Ni(dpdo)I$_2$] (3.16—3.61 Å) are longer on average than those in [Ni(dpdo)(NCS)$_2$] [3.063(7) and 3.19(7) Å].

The structure of [Ni(dpdo)(NCS)$_2$] establishes that the ligand dpdo can bridge *trans* positions at square-planar nickel(II) without adopting an energetically unfavourable conformation and with only moderate distortion of the metal valency angles.

We have isolated a number of complexes which include solvent molecules. These give further evidence of the diverse co-ordination abilities of facultative potentially quadridentate ligands. The blue complex [Ni(dpdo)Br$_2$]·C$_6$H$_5$Me may be isolated from reaction in toluene. This diamagnetic material may be planar in the solid state {*cf.* the unsolvated [Ni(dpdo)Br$_2$] which is pseudotetrahedral}. In solution, the spectra of both the solvated and unsolvated complex indicate planar geometry, Table 2.

The structures of the remaining two complexes cannot be assigned with any degree of certainty in the absence of crystal structures. The orange diamagnetic planar [Ni(dpdo)(H$_2$O)$_2$][BF$_4$]$_2$ is a 1 : 2 electrolyte in both methylene chloride and nitromethane and the molecular weight in chloroform (Found: 230. Calc.: 754 for a non-conducting monomer) confirms this. Moreover, the intense single i.r. band at 1 060 cm^{-1} is evidence for the free tetrahedral BF$_4^-$ anion. No shift in ν(COC) is observed from the free ligand and so we tentatively suggest that the dpdo ligand acts as a *trans*-chelating bidentate phosphine species in [Ni(dpdo)(H$_2$O)$_2$][BF$_4$]$_2$. Both the electronic reflectance spectrum and the room-temperature magnetic moment of the turquoise Ni(dpdo)(H$_2$O)$_4$Cl$_2$ complex indicate octahedral geometry. In halogenocarbon solvents the spectrum of this complex is identical to the anhydrous planar [Ni(dpdo)Cl$_2$]. Additional evidence for this formulation comes from the non-electrolyte nature of the complex in halogenocarbons. The ν(COC) band at 1 110 cm^{-1} of free dpdo shifts to lower energy, 1 070 cm^{-1}, in Ni(dpdo)(H$_2$O)$_4$Cl$_2$, indicating co-ordination of the ether oxygens of the ligand. The evidence thus suggests that this complex can best be described as [Ni(dpdo)Cl$_2$]·4H$_2$O and that the structures in the solid state and in halogenocarbons of the co-ordination entity are as shown below. This behaviour can be contrasted with that of [NiLCl$_2$] [L is the diarsine dithioether chelate 1,3-bis(3′-dimethylarsinopropylthio)propane] which has a similar *trans*-octahedral structure in the solid state (NiAs$_2$S$_2$Cl$_2$ donor set) but becomes a planar [NiLCl$_2$](NiAs$_2$S$_2$ donor set) species in solution.[26] However, this As$_2$S$_2$ ligand does co-ordinate as a bidentate As$_2$ ligand in *trans*-[MLX$_2$] (M = Pd or Pt; X = Cl, Br, or I).[9,13]



In conclusion, we would like to once again emphasize the diverse properties of these facultative ligands which can act either as a quadridentate or as a *trans*-bidentate ligand.

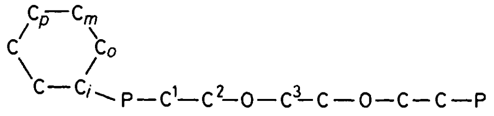
EXPERIMENTAL

Reagents.—The nickel(II) salts, diphenylphosphinous chloride, and the solvents were reagent grade and were used without further purification. The solvent, di-n-butyl ether, was dried before use by distilling from sodium and benzophenone.

Preparation of the Ligand.—All operations were carried out under dry nitrogen with oxygen-free solvents. Slivers of sodium metal (15 g, 0.650 mol) in di-n-butyl ether (200 cm^3) were heated and at the reflux temperature (140 °C) were converted into sodium sand by vigorous stirring. Stirring was continued while diphenylphosphinous chloride (35 g, 0.160 mol) in di-n-butyl ether (70 cm^3) was added dropwise over 1 h. Reflux and stirring were maintained for another 3 h.

When cool, the yellow sodium diphenylphosphide slurry was transferred to a 500-cm^3 flask. The dibromide, 1,8-dibromo-3,6-dioxaoctane (20.7 g, 0.075 mol), in di-n-butyl ether (50 cm^3) was added dropwise and stirring was maintained for another 1 h.

The mixture was filtered to remove sodium halide salts and the filtrate was evaporated to dryness under reduced pressure. The crude product was recrystallized from either hexane or ethanol, m.p. 55.5—56.0 °C (Found: C, 71.7; H, 6.4. Calc. for $C_{30}H_{32}O_2P_2$: C, 74.1; H, 6.6%); $\delta(^1H)$ (p.p.m., $CDCl_3$, internal standard $SiMe_4$) 2.20 (t, PCH_2CH_2O and OCH_2CH_2P), 3.40 (m, OCH_2CH_2O), 7.30 (m, C_6H_5); $\delta(^{31}P)$ (p.p.m., $CDCl_3$, external standard 85% phosphoric acid) 21.8; $\delta(^{13}C)$ ($CDCl_3$, internal standard $SiMe_4$) −29.2 [*J*(P–C) 13.9 Hz, C^1], −68.7 [*J*(P–C) 24.6 Hz, C^2], −70.2 (C^3), −128.3 (C–P), −128.6 (*m*-C), −122.7 [*J*(P–C) 19.1 Hz, *o*-C], and −138.8 [*J*(P–C) 13.6 Hz, *i*-C].



Preparation of the Complexes.—The complexes [Ni(dpdo)X_2] (X = Cl, Br, I, or NCS) were prepared by dissolving the appropriate anhydrous nickel(II) salt (2 mmol) in absolute ethanol (30 cm^3). The ligand (1.00 g, 2 mmol) dissolved in absolute ethanol (20 cm^3) was mixed with the salt solution and stirred for 30 min. The complexes were filtered off and washed with ethanol. The chloro- and bromo-complexes were hydroscopic in nature and were not purified further. The iodo- and thiocyanato-complexes were recrystallized from a chloroform–ethanol (1 : 1) solution.

The hydrated complex [Ni(dpdo)Cl_2]·4H_2O was prepared by treating [Ni(H_2O)$_6$]Cl_2 with the ligand in a 1 : 1 molar ratio as above. The resulting solution was filtered and the mother-liquor was concentrated by evaporation under reduced pressure. The crystalline turquoise complex was filtered off and washed with ethanol.

The solvated complex [Ni(dpdo)Br_2]·C_6H_5Me was prepared by recrystallizing the bromo-complex from a toluene solution. The dark blue crystalline complex was filtered off and washed with small portions of pentane.

The hydrated complex [Ni(dpdo)(H_2O)$_2$][BF_4]$_2$ was prepared by treating [Ni(H_2O)$_6$][BF_4]$_2$ (0.68 g, 2 mmol) and the ligand (1.00 g, 2 mmol) in refluxing benzene (30 cm^3) with 2,2-dimethoxypropane (5 cm^3), present as a water scavenger. Reflux was maintained for 30 min after which the benzene was evaporated to dryness under reduced pressure. The orange complex was recrystallized from a chloroform–benzene (2 : 1) solution, filtered off, and washed with small portions of dry pentane.

All the complexes were collected by vacuum filtration on sinter-glass filters and were dried under vacuum.

Physical Measurements.—The proton n.m.r. spectrum of the ligand was recorded on a Varian EM 390 spectrometer at a frequency of 90 MHz, and the ^{13}C and ^{31}P n.m.r. spectra on a Varian CFT 20 Fourier-transform spectrometer. Magnetic-moment data for the complexes were obtained by the Gouy method using Hg[Co(SCN)$_4$] as calibrant. Diffuse reflectance and solution electronic spectra were recorded on a Cary 17 spectrophotometer. Molecular weights were determined in chloroform by vapour-phase osmometry. The i.r. spectra were recorded on a Perkin-Elmer 580 spectrometer as Nujol mulls between KBr plates; a polyethylene cell was used for the low-energy solution i.r. spectra. Conductivity measurements were made using a platinum electrode dipping cell and a conductivity bridge.

X-Ray Analysis.—*Crystal data.* $C_{32}H_{32}N_2NiO_2P_2S_2$, *M* = 661.4, Orthorhombic, *a* = 10.102(2), *b* = 10.695(2), *c* = 30.010(4) Å, *U* = 3 242 Å^3, *Z* = 4, D_c = 1.355 g cm^{-3}, *F*(000) = 1 376, space group $P2_12_12_1$, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 8.5 cm^{-1}.

An Enraf–Nonius CAD-4F diffractometer equipped with a graphite monochromator was used in conjunction with Mo-K_α radiation. The specimen was a red needle of dimensions 0.55 × 0.28 × 0.35 mm. The cell dimensions were obtained from a least-squares fit to the setting angles of 25 automatically centred reflections. The integrated intensities of all independent reflections in the range $3 \leqslant \theta \leqslant 30°$ were estimated from continuous θ—2θ scans of 0.90° in θ, the scan speed being adjusted to give $\delta(I)/I \leqslant 0.02$, subject to a maximum counting time of 80 s. Correction for background and Lorentz polarization effects yielded 2 146 reflections with $I \geqslant 3\sigma(I)$.

Structure analysis. The structure was solved and refined using conventional Patterson, difference-Fourier, and least-squares techniques. The phenyl rings were constrained to be hexagons of side 1.395 Å. In the later calculations fixed contributions for the hydrogen atoms were added to the structure factors, the hydrogen positions being deduced geometrically, assuming C–H 1.00 Å. Anisotropic thermal parameters were used for all but the hydrogen and phenyl carbon atoms. The function minimized was $\Sigma w(|F_o| -$

TABLE 6

Fractional co-ordinates of non-hydrogen atoms
(× 10^5 for Ni, × 10^4 otherwise)

Atom	*x*	*y*	*z*
Ni	15 290(11)	16 155(10)	12 399(3)
S(1)	−1 559(3)	−1 065(3)	667(1)
S(2)	3 368(5)	4 945(3)	1 962(1)
P(1)	2 577(2)	2 411(2)	646(1)
P(2)	622(3)	828(2)	1 858(1)
O(1)	4 232(7)	386(6)	1 091(2)
O(2)	2 515(8)	−1 122(7)	1 501(3)
N(1)	425(6)	546(8)	936(2)
N(2)	2 373(9)	2 861(7)	1 546(2)
C(1)	−411(10)	−117(9)	822(3)
C(2)	2 771(11)	3 746(8)	1 722(4)
C(3)	4 397(9)	2 321(10)	730(3)
C(4)	4 862(11)	989(11)	743(4)
C(5)	4 463(11)	−899(10)	1 094(5)
C(6)	3 828(12)	−1 449(12)	1 506(5)
C(7)	1 814(13)	−1 470(9)	1 881(4)
C(8)	457(11)	−870(8)	1 876(3)
C(11)	2 390(6)	1 758(5)	92(1)
C(12)	2 946(6)	504(5)	39(1)
C(13)	2 002(6)	−22(5)	−386(1)
C(14)	2 303(6)	706(5)	−758(1)
C(15)	2 648(6)	1 960(5)	−705(1)
C(16)	2 692(6)	2 486(5)	−280(1)
C(21)	2 225(7)	4 054(5)	587(2)
C(22)	899(7)	4 410(5)	561(2)
C(23)	565(7)	5 673(5)	530(2)
C(24)	1 558(7)	6 579(5)	534(2)
C(25)	2 884(7)	6 223(5)	549(2)
C(26)	3 218(7)	4 961(5)	581(2)
C(31)	1 377(6)	1 166(5)	2 393(2)
C(32)	604(6)	1 151(5)	2 778(2)
C(33)	1 179(6)	1 412(5)	3 190(2)
C(34)	2 526(6)	1 688(5)	3 217(2)
C(35)	3 299(6)	1 703(5)	2 832(2)
C(36)	2 724(6)	1 442(5)	2 420(2)
C(41)	−1 040(5)	1 416(5)	1 891(2)
C(42)	−2 146(5)	639(5)	1 867(2)
C(43)	−3 415(5)	1 152(5)	1 878(2)
C(44)	−3 577(5)	2 444(5)	1 912(2)
C(45)	−2 471(5)	3 222(5)	1 930(2)
C(46)	−1 242(5)	2 748(5)	1 926(2)

$|F_c|)^2$ with $1/w = \sigma^2 + (0.02F_o)^2$, where σ was the standard deviation of $|F_o|$ derived solely from counting statistics. Refining of 203 parameters converged at R 0.050 and R' 0.055. Corresponding values for the enantiomeric model (R 0.057 and R' 0.062) were significantly higher. The final difference synthesis was featureless ($|\Delta_o| < 0.6$ e Å^{-3}) and the weighting analysis satisfactory. Scattering factors and anomalous dispersion corrections were taken from ref. 27. Programs used were local modifications of SHELX 78 (G. M. Sheldrick), CAD4 (M. B. Hursthouse), ORTEP (C. K. Johnson), and P. R. Mallinson's GEOM.

Final atomic co-ordinates for non-hydrogen atoms are given in Table 6. Supplementary Publication No. SUP 23229 (14 pp.) contains observed and calculated structure factors and atomic vibrational parameters.*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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