Notes

Preparation and Spectroscopic Characterization of Pseudo-tetrahedral $[NiX_2\{Ph_2P(CH_2)_8PPh_2\}]$ (X = Cl, Br, or I) and Planar $[Ni(NCS)_2\{Ph_2P(CH_2)_8PPh_2\}]$ †

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The long-chain diphosphine 1,8-bis(diphenylphosphino)octane, dpo, forms pseudo-tetrahedral $[Ni(dpo)X_2]$ complexes (X = Cl, Br, or I). Molecular-weight data indicate that $[Ni(dpo)I_2]$ is dimeric in chloroform, and thus contains bridging bidentate diphosphine ligands. The complex $[Ni(dpo)(NCS)_2]$ is diamagnetic and square planar. The donor properties of dpo are compared to those of 1,8-bis(diphenylphosphino)-3,6-dioxaoctane, a potentially P_2O_2 donor ligand.

FOUR-CO-ORDINATE nickel(II) complexes are usually square planar, although bulky ligands or those with weak ligand-field strengths can promote tetrahedral geometry. In recent years, new interest in the geometry of simple co-ordination complexes has been generated by the synthesis of complexes of long-chain bidentate ligands.

The first example of *trans* chelation by a long-chain bidentate ligand was claimed [1] for $[Ni\{(C_6H_{11})_2P(CH_2)_5P(C_6H_{11})_2\}Br_2]$, but for a pentamethylene chain the structure must be severely distorted from square planar.[2] In 1976, Shaw and co-workers [3] prepared complexes of the type *trans*-$[\{M[Bu^t_2P(CH_2)_nPBu^t_2]Cl_2\}_x]$ (M = Pd or Pt; n = 8, 9, 10, or 12; x = 1, 2, or 3) by the reaction of *trans*-$[M(PhCN)_2Cl_2]$ with the appropriate ligand in refluxing 2-methoxyethanol or toluene. The mononuclear complexes could be sublimed at 185—195 °C and 1 atm ‡ pressure without decomposition. Shaw suggested that the *trans* configuration adopted by these ligands is due to the bulky t-butyl groups; these substituents produce favourable conformational effects in the *trans* configuration, whereas the *cis* geometry is excluded because of steric overcrowding. However, a series of complexes which have been assigned *trans* configurations but which do not have terminal t-butyl substituents include $[\{Pd[Ph_2P(CH_2)_nPPh_2]X_2\}_x]$ (n = 6, 8, 10, or 12; x = 1 or 2; X = Cl, Br, I, or NCS),[4] $[Pd\{Me_2As(CH_2)_{12}AsMe_2\}Cl_2]$,[5] $[M\{PhS(CH_2)_{12}SPh\}X_2]$ (M = Pd or Pt; X = Cl or Br),[6] and $[MLX_2]$ (M = Ni, Pd, or Pt; X = Cl, Br, or I) where L is the ligand with the rigid planar backbone, 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene.[7]

We have recently become interested in potentially quadridentate open-chain chelating ligands of the type $Me_2As(CH_2)_3S(CH_2)_3S(CH_2)_3AsMe_2$ which can adopt a variety of configurations around nickel(II), palladium(II), and platinum(II).[8] A closely related system is that provided by the ligand 1,8-bis(diphenylphosphino)-3,6-dioxaoctane, $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$, dpdo, which Dapporto and Sacconi [9] showed to act as a P_2 donor system in the distorted square-planar diamagnetic complex $[Ni(dpdo)I_2]$. We have extended [10] this investigation of dpdo, and have also examined the co-ordination properties of $Ph_2P(CH_2)_8PPh_2$ (dpo) towards nickel(II). Here, we report our studies with dpo, which complement the previous studies of dpdo, since both ligands have eight intermediate atoms between the two phosphorus donors.

EXPERIMENTAL

Materials.—The anhydrous nickel(II) salts and solvents were all reagent grade and were used without further purification. The ligand, dpo, was prepared as described previously.[4]

Preparation of the Complexes.—The complexes $[Ni(dpo)X_2]$ (X = Cl, Br, or I) were prepared by refluxing the appropriate anhydrous nickel halide salt (2 mmol), the ligand dpo (1.00 g, 2 mmol), and 2,2-dimethoxypropane (1 cm^3) in n-butanol (30 cm^3). After refluxing for *ca.* 2 h, the solution was vacuum filtered while hot. The residue was washed with portions (2 × 10 cm^3) of methylene chloride. The combined filtrates were concentrated under reduced pressure. On cooling, the precipitated complex was collected by vacuum filtration, washed with portions (2 × 10 cm^3) of absolute ethanol, and dried under vacuum.

The complex $[Ni(dpo)(NCS)_2]$ was prepared by dissolving anhydrous nickel(II) thiocyanate (0.36 g, 2 mmol) and dpo (1.00 g, 2 mmol) in absolute ethanol (30 cm^3) and stirring for 12 h. The orange product was collected by vacuum filtration and purified by extraction with chloroform in a Soxhlet apparatus.

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 580 spectrometer using KBr plates (600—4 000 cm^{-1}, hexachlorobutadiene and Nujol mulls) and polyethylene plates (200—600 cm^{-1}, Nujol mulls). Electronic spectra were obtained on a Cary-17 spectrometer. Magnetic moments were determined by the Gouy method using $Hg[Co(NCS)_4]$ as calibrant. The molecular weight in chloroform was determined by osmometry.

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† [1,8-Bis(diphenylphosphino)octane]bis(isothiocyanato)-nickel(II).

‡ Throughout this Note: 1 atm = 101 325 Pa.

RESULTS AND DISCUSSION

The ligand dpo was prepared by the reaction of $LiPPh_2$ with $Br(CH_2)_8Br$, and the complexes $[Ni(dpo)X_2]$ were isolated from the reaction of NiX_2 with dpo in refluxing n-butanol (X = Cl, Br, or I) or absolute ethanol (X = NCS). Table 1 contains elemental analyses and some physical properties of the complexes.

TABLE 1

Elemental analyses, magnetic moments, and infrared data of the complexes

Complex	Colour	Analysis (%) [a] C	H	X	$\mu_{eff.}(\mu_B)$	I.r. bands/cm^{-1} ν(Ni–P) [b]	ν(Ni–X)
$[Ni(dpo)Cl_2]$	Purple	63.1(62.8)	5.4(5.9)	10.7(11.6)	2.48	225w 250w	295m 335m
$[Ni(dpo)Br_2]$	Olive green	54.3(54.8)	5.0(5.2)	23.3(22.8)	3.11	200w	225m 257m
$[Ni(dpo)I_2]$ [c]	Brown	48.6(48.3)	4.6(4.6)	32.1(31.9)	3.24		
$[Ni(dpo)(NCS)_2]$ [d]	Orange	62.2(62.1)	5.6(5.5)	3.9(4.3) [e]			

[a] Calculated values are given in parentheses. [b] Tentative assignment. [c] Molecular weight in chloroform 1 539 (795 calculated for the monomer). [d] ν(CN) at 2 092s cm^{-1}. [e] X = N.

The $[Ni(dpo)X_2]$ (X = Cl, Br, or I) complexes exhibit electronic spectra (Table 2) which are indicative of pseudo-tetrahedral geometry in the solid state (Figure 1) and in solution in methylene chloride (Figure 2). In general, tetrahedral nickel(II) complexes have multiple visible absorption bands. The ν_3 transition occurs near 16 000 cm^{-1} and is assigned to $^3T_1(P)\leftarrow{}^3T_1$. Weak bands, on the low-energy and high-energy side of the intense band, have been assigned to spin-forbidden transitions to components of the ^1D and ^1G levels respectively. The absorption at *ca.* 8 000 cm^{-1} is the ν_2 transition, $^3A_2\leftarrow{}^3T_1$, and the ν_1 transition derives from $^3T_2\leftarrow{}^3T_1$. In the spectra (Figures 1 and 2) all of the expected transitions for NiP_2X_2 systems which have been assigned pseudo-tetrahedral geometry occur. In particular, the energy and intensity of the bands are very close to those of the $[Ni(PPh_3)_2X_2]$ (X = Cl, Br, or I) complexes, which are known to have a pseudo-tetrahedral structure.[11,12] As expected, a decrease in energy of the ν_3 and ν_2 transitions occurs on going from the chloro-, to the bromo-, to the iodo-complex, reflecting the decrease in the ligand-field strength of the halide donors. In contrast to the halogeno-complexes, the solid-state reflectance spectrum of $[Ni(dpo)(NCS)_2]$ is indicative of planar geometry, Figure 1.

The room-temperature magnetic moments of $[Ni(dpo)X_2]$ in the solid state, $\mu_{eff.} = 3.11\ \mu_B$ (X = Br) and $3.24\ \mu_B$ (X = I), are consistent with a pseudo-tetrahedral structure with low orbital contribution. Several preparations of $[Ni(dpo)Cl_2]$ always resulted in a complex for which $\mu_{eff.} = 2.48\ \mu_B$. We suggest that this complex may represent a spin-crossover system, since there is no evidence in the electronic spectra for any diamagnetic planar isomer. Low solubility prevented us obtaining solution magnetic moments by the method of Evans.[13] As expected, the planar $[Ni(dpo)(NCS)_2]$ complex was diamagnetic.

TABLE 2

Data from the reflectance and solution electronic spectra of the complexes

Complex	Solid $10^{-3}\ \lambda_{max.}$/cm^{-1}	Absorbance	Solution * $10^{-3}\ \lambda_{max.}$/cm^{-1}	ϵ/dm^3 mol^{-1} cm^{-1}
$[Ni(dpo)Cl_2]$	27.1	1.26	27.1	3 182
	19.5	0.84	19.5	325
	11.5	0.14	11.7	51
	9.2	sh		
	5.9	0.08		
$[Ni(dpo)Br_2]$	24.6	0.70	25.2	3 300
	17.2	0.55	17.9	900
	11.3	0.75	11.7	90
	9.3	sh		
	5.6	0.10		
$[Ni(dpo)I_2]$	23.3	1.20	23.4—26.4	3 500
	15.6	sh	15.6	sh
	10.8	0.75	10.9	270
	5.8	0.05		
$[Ni(dpo)(NCS)_2]$	26.2	1.30		
	22.7	sh		

* Solvent = methylene chloride.

The i.r. spectra of $[Ni(dpo)X_2]$ (X = Cl or Br) contain bands which offer additional evidence for pseudo-tetrahedral geometry; the ν(Ni–P) and ν(Ni–X) absorptions occur at energies similar to those previously assigned for this geometry,[14-16] Table 1. The i.r. spectrum of $[Ni(dpo)(NCS)_2]$ in the solid state exhibits one broad band at 2 092 cm^{-1} assignable to ν(CN) of Ni–NCS linkages.[17]

Due to low solubility of the chloro- and bromo-complexes, it was not possible to obtain reliable molecular-weight data for the complexes. However, [Ni-

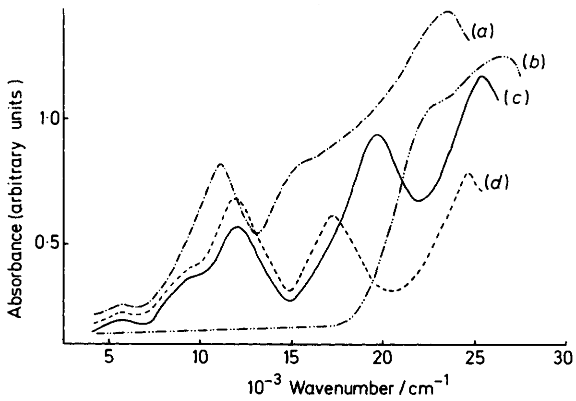

FIGURE 1 Reflectance spectra of the complexes [Ni(dpo)X_2], X = I (*a*), NCS (*b*), Cl (*c*), and Br (*d*)

(dpo)I_2] was appreciably more soluble and a molecular-weight determination in chloroform is consistent with a dimeric structure (Found: 1 539. Calc.: 1 590), Figure 3. It is likely that the complexes [Ni(dpo)X_2] (X = Cl or Br) are also pseudo-tetrahedral dimers. All of the complexes reported here are non-electrolytes in chloroform.

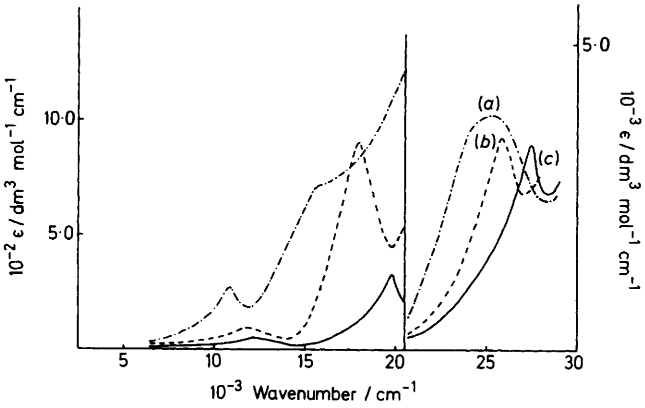

FIGURE 2 Solution spectra of the complexes [Ni(dpo)X_2], X = Br (*a*), Cl (*b*), and I (*c*)

We are thus in a position to compare the donor properties towards nickel(II) of the two ligands, dpdo and dpo, both of which have terminal Ph_2P groups bridged by eight linking atoms: *i.e.* $Ph_2P(CH_2)_2O(CH_2)_2$-$O(CH_2)_2PPh_2$ (dpdo) and $Ph_2P(CH_2)_2CH_2(CH_2)_2CH_2$-$(CH_2)_2PPh_2$ (dpo). Despite the fact that there is no evidence for co-ordination of the ether functions of dpdo in [Ni(dpdo)X_2] (X = I or NCS), as shown by *X*-ray crystal structures,[9,10] it is clear that the presence of the non-co-ordinating ether function instead of a non-co-ordinating methylene group in the backbone of these $Ph_2PY_8PPh_2$ ligands has a significant effect on the co-ordinating properties of the ligands. Thus, the complexes [Ni(dpdo)X_2] (X = Cl or Br) are pseudo-tetrahedral in the solid but planar in methylene chloride, whereas for X = I or NCS, planar monomeric geometry is present in both solid and solution.[9] However, for dpo our evidence suggests that the complexes [Ni(dpo)X_2] (X = Cl, Br, or I) are tetrahedral dimers, while [Ni(dpo)$(NCS)_2$] is planar. In all cases, both ligands act as bidentate diphosphines. It is clear that the nature of the chelate effect in long-chain bidentate/quadridentate ligands needs much more investigation. This is further illustrated by the isolation and *X*-ray crystal-structure determinations of the monomeric complexes *cis*-[Pd(dpdo)Cl_2] and *trans*-[Pd(dpdo)I_2];[18] the former contains the first example of an 11-membered ring containing a *cis*-bidentate monomeric species.

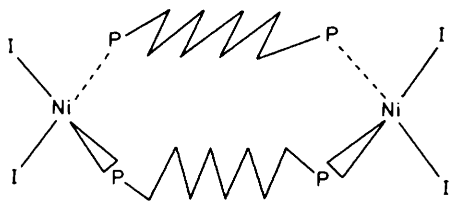

FIGURE 3 Proposed binuclear structure of [Ni(dpo)I_2]

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