A Paramagnetic 1:1 Adduct of Triphenylphosphine and Bis(diethyldithiophosphato)nickel(II)

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Summary Square planar bis(diethyldithiophosphato)-nickel(II) forms a stable, paramagnetic, 1:1 adduct with triphenylphosphine which in solution undergoes rapid triphenylphosphine exchange.

ALTHOUGH a variety of bases are known to form both 1:1 and 2:1 adducts in solution with square planar bis(dialkyl dithiophosphato)nickel(II), only 2:1 six co-ordinate adducts have been isolated and characterized.[1–4] The six co-ordinate adducts have been the subject of a number of recent spectroscopic investigations.[1] We report that triphenylphosphine reacts readily with $Ni(dtp)_2$, [dtp = $(EtO)_2PS_2^-$] to form dark green crystals of the first example of a 1:1, five co-ordinate adduct of $Ni(dtp)_2$ isolated in the solid state, $K_1 = 1{\cdot}2 \pm 0{\cdot}3$ l mol^{-1}, ϵ (6000 Å) = 154 ± 5.

All attempts to prepare the 2:1 adduct failed. A spectral analysis indicated that only a 1:1 adduct is formed in solution with metal:triphenylphosphine mole ratios of up to 470:1. The ease with which the 1:1 complex could be isolated is in marked contrast with the impossibility of isolating the amine adducts[3] and probably results from a particularly stable crystal lattice in our compound.

When dissolved in common organic solvents, $Ni(dtp)_2$-PPh_3 undergoes immediate partial dissociation into $Ni(dtp)_2$ and free triphenylphosphine. Three isosbestic points between 9000 and 12,000 Å in the visible absorption spectrum of $Ni(dtp)_2$ in acetone with varying mole ratios of excess triphenylphosphine provide good evidence for the existence of only $Ni(dtp)_2$ and its 1:1 adduct in solution. Most 2:1 adducts absorb strongly in this region.[1]

The structure of $Ni(dtp)_2PPh_3$ is most probably a distorted square pyramid with the nickel above the plane of the sulphur atoms. This is expected on the basis of the strong metal sulphur π-interaction and the weak nickel–PPh_3 interaction.[2] A distorted square-pyramidal structure was assigned to the di-n-butylamine adduct in solution by Jorgensen.[3] The i.r. and u.v. spectral data support but do not prove the validity of the above predictions. The P–S and P–O stretching frequencies (Table) increase slightly upon co-ordination as would be expected if π-back donation

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TABLE

Spectral and magnetic properties

Compound	$\chi \times 10^6$ cgs[a]	μ_{eff}(BM)	ν_{P-S}[b] (cm^{-1})	ν_{P-O} (cm^{-1})	Electronic absorption (cm^{-1})		
					obs.	calcd.[c]	assignment
Ni(dtp)$_2$	diamag.	diamag.	536	1155	15,600		$^1A_{1g} \rightarrow {}^1B_1$
			641		19,200		$\rightarrow {}^1A_2$
Ni(dtp)$_2$PPh$_3$	3242	2·79	543	1158	8710	8000	^3B, $\rightarrow {}^3E$
			663		11,300	11,500	$\rightarrow {}^3A_2$
					13,500	13,200	$\rightarrow {}^3B_2$
					17,300	18,000	$\rightarrow {}^3E$

[a] Measured at 25 °C by the Faraday Method. [b] KBr pellets. [c] Calculated for P–Ni–S angle of 100° and an effective ligand dipole moment of 5·2D.

from the metal is decreased by pushing the plane of the sulphurs below the nickel. No new bands are observed as would be expected in a trigonal bipyramidal configuration with three equatorial and one axial sulphur. The electronic absorption spectrum is not an absolute diagnostic means of determining between the limiting geometries since both configurations are expected to give rise to six bands. A tentative structural assignment may be made by attempting to fit the observed absorption spectrum to one calculated using the splitting diagrams for square pyramidal geometry.[5] The observed and calculated transition energies and their tentative assignments are shown in the Table. No fit could be obtained using the diagram for trigonal bipyramidal geometry.

The 1:1 adduct is paramagnetic in both the solid state and in solution. The n.m.r. spectrum is characteristic of an ethyl group split by the spin $\frac{1}{2}$ ^{31}P nucleus and contact-shifted upfield by the unpaired electron density from the paramagnetic metal. The magnitude of the upfield shift increases as excess triphenylphosphine is added as would be expected for rapid exchange. A complete magnetic resonance kinetic study is in progress on this system.

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