Inorganica Chimica Acta, 17 (1976) 5–11

Transition Metal Complexes of Organothiophosphorus Ligands. III[a]. Six-coordinate Adducts of Nickel(II)bis(Diphenylphosphorodithioate) with Aromatic and Heterocyclic Diamines

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Received February 7, 1975

Nickel(II)bis(diphenylphosphorodithioate), $Ni[S_2P(OC_6H_5)_2]_2$, forms several types of six-coordinate adducts with aromatic primary diamines (o,o'- and p,p'-diaminobiphenyl, 2,7-diaminofluorene, o- and p-phenylenediamine) and heterocyclic diamines (orthophenanthroline, 2,2'-bipyridyl). Two isomers of $Ni[S_2P(OPh)_2]_2\cdot 2o$-PHDA were isolated. All compounds were characterized by elemental analysis, electronic and infrared spectra and magnetic moments. Possible structures are discussed on the basis of these data.

Introduction

Transition metal complexes with phosphorodithioate groups as ligands are intensively investigated in recent years[1], as a part of the general attention given to complexes of sulphur-containing ligands[2]. The points of interest which prompted our attention for this type of compounds can be resumed as follows:

a) Phosphorodithioates form four-membered chelate rings, which exhibit the peculiarity of not containing any carbon atom in the ring. Thus, we have a particular type of inorganic ring systems[3,4] (purely inorganic chelate metallocycles), which are only at the beginning of their exploration.

b) Interesting and unusual coordination geometries are sometimes achieved, by formation of phosphorodithioate metal chelate adducts with additional ligands (amines, phosphines)[1], *e.g.* five-coordination of nickel.

c) Biological activity may be expected for some transition metal phosphorodithioates[5].

d) Phosphorodithioate chelates and salts are useful as lubricant additives, stabilizers, anticorrosive agents, or are used in flotation of metal ores[1]. Their solubility in organic solvents makes them also useful in solvent extraction of metals. New uses can be expected for these compounds.

The chemistry of transition metal phosphorodithioates was authoritatively reviewed in recent years[1]. The most intensively investigated were the nickel(II) chelates $Ni[S_2P(OR)_2]_2$; these are square planar compounds and they are able to form five- and six-coordinate adducts $Ni[S_2P(OR)_2]_2\cdot nL$ ($n = 1$ or 2). In general the amine adducts exhibit moderate stability, especially when L is an alkylamine, and sometimes the adduct cannot be isolated from solution or readily loses the amine on standing in open atmosphere. Most of the adducts studied were those of nickel(II) bis(diethylphosphorodithioate).

We prepared and investigated some adducts of nickel(II)bis(diphenylphosphorodithioate) with aromatic and heterocyclic diamines, with the assumption that bulky aromatic groups may influence their structure and behaviour, and with the hope that non-volatile amines will have an unfavourable effect upon the shift of the dissociation equilibrium. A similar investigation was performed with nickel(II)bis(dialkylphosphorodithioates) and will be published later[6].

Experimental

Materials and Methods

The reagents used were of analytical grade purity. Diphenylphosphorodithioic acid, $(PhO)_2P(S)SH$, has been prepared according to a known procedure[7].

Infrared spectra were recorded in KBr pellets on a UR-20 Carl Zeiss Jena instrument and electronic spectra (diffuse reflectance) on a VSU-2G Carl Zeiss Jena instrument, sometimes in MgO diluted pellets. Magnetic moments were determined on a Faraday balance at room temperature and were corrected for the diamagnetism of the ligands.

The metal content was determined as Ni(II)bis(dimethylglyoximate) and phosphorus as ammonium 12-molybdophosphate (gravimetrically). Nitrogen was determined by combustion (micro-Dumas).

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Preparation of Ni(II)bis(diphenylphosphorodithioate), $Ni[S_2P(OPh)_2]_2$

A solution of diphenylphosphorodithioic acid in chloroform was treated with an excess of concentrated aqueous solution of Ni(II) acetate. The solutions were stirred together until inter-phase equilibrium was achieved and the organic layer was then separated in a separatory funnel. The dark purple solution was concentrated and the solid was filtered and recrystallized from chloroform, to give a crystalline purple solid, m.p. 109–111° C. Found: Ni 9.63, P 9.65%; Calcd. for $C_{24}H_{20}O_4S_4P_2Ni$: Ni 9.45, P 9.98%.

Preparation of the 1:1 Diamine Adducts I–VI (Table I)

Several 1:1 adducts of the following amines were prepared: *p*-phenylenediamine (*p*-PHDA), *o,o'*- and *p,p'*-diaminobiphenyl (*o,o'*- and *p,p'*-DABP), 2,7-diaminofluorene (2,7-DAF), orthophenanthroline (PHEN) and 2,2'-dipyridyl (DIPY). The following general procedure was used: Nickel(II)bis(diphenylphosphorodithioate) (0.60 g) dissolved in 10 ml acetone was treated with the calculated amount of the amine in acetone, as required by the 1:1 ratio. The adducts usually precipitated immediately, sometimes after concentration of the solution and were filtered, washed with ethanol and diethylether and dried. The compounds thus prepared are listed in Table I under numbers I–VI. In the synthesis of compounds III and V this procedure gave viscous gums, from which the crystalline adducts were obtained by treatment with dimethylformamide, followed by evaporation.

Preparation of $Ni[S_2P(OPh)_2]_2 \cdot 2$ o-PHDA (Green Isomer VII)

All attempts to obtain a 1:1 adduct of *o*-phenylenediamine (*o*-PHDA) according to the above procedure gave a green compound which analysed for the 1:2 adduct. Other procedures used to obtain the 1:2 adduct are described below.

A mixture of 0.60 g $Ni[S_2P(OPh)_2]_2$ in 10 ml acetone and 0.2 g *o*-PHDA in 5 ml acetone was concentrated to leave a viscous gum. The crystalline 1:2 adduct was isolated by treating it with a mixture of petroleum ether–benzene–dimethylformamide (approx. 1:1:1 in volume) which induced crystallization. This procedure is not easily reproducible.

A much better procedure, easy to reproduce if freshly prepared $Ni[S_2P(OPh)_2]_2$ and very pure reagents are used, was the following: stoichiometric amounts of $Ni[S_2P(OPh)_2]_2$ and *o*-PHDA were mixed dry in a mortar, then 3–5 ml of diethylether was added. The green solid formed was filtered immediately and dried.

If grinding in the mortar was continued, the green compound was gradually converted into a pink–purple isomer, which can also be prepared as described below.

Preparation of $Ni[S_2P(OPh)_2]_2 \cdot 2$ o-PHDA (Pink–Purple Isomer VIII)

The green viscous gum formed as described above in the preparation of compound VII was treated with a 1:3 dimethylformamide–water mixture and stirred. After *ca.* 0.5 hr the pink–purple isomer was separated, washed with water, ethanol and ether, then dried. It can be recrystallized from absolute ethanol.

The green and pink–purple isomers are interconvertible. Thus, the pink–purple isomer can be dissolved in acetone, and evaporation of the green solution formed yields a green viscous gum as mentioned in the preparation of compound VII.

The green compound VII melts at 163–165° C and the melt has the same colour. The pink–purple isomer VIII melts at 170° C and the melt is green. Also, on heating at ~145° C for several hours, the pink–purple compound VIII is converted into the green isomer VII.

Preparation of $Ni[S_2P(OPh)_2]_2 \cdot 3$ o-PHDA (IX)

A slight excess of *o*-PHDA in a synthesis performed under the same conditions as for the preparation of compound VIII gives a blue compound, the analysis of which indicates a 1:3 adduct. On long standing, or better on heating to 120° C the 1:3 adduct loses one molecule of amine to yield the pink–purple compound VIII described above. Further heating at ~145° C gives the green isomer VII.

Preparation of $Ni[S_2P(OPh)_2]_2 \cdot 3$PHEN (X)

Attempts to prepare the 1:2 adduct gave only the 1:3 adduct even when the stoichiometric ratio was used. A solution of 0.6 g PHEN in 10 ml acetone mixed with a solution of 0.6 g $Ni[S_2P(OPh)_2]_2$ in 10 ml acetone deposited a pink microcrystalline precipitate, which was filtered, washed with alcohol and ether and dried.

Preparation of $Ni]S_2P(OPh)_2]_2 \cdot 3$DIPY (XI)

This compound was prepared analogously to compound X.

All compounds prepared, some of their properties and analytical data are given in Table I.

Results and Discussion

The reactions of Ni(II)bis(diphenylphosphorodithioate) with aromatic and heterocyclic diamines yield various types of adducts. The electronic spectra and magnetic data discussed below show that all of them contain six-coordinate nickel. Therefore, in the 1:1 adducts obtained with *p,p'*-diaminobiphenyl (*p,p'*-DABP), *o,o'*-diaminobiphenyl (*o,o'*-DABP), 2,7-diaminofluorene (2,7-DAF), *p*-phenylenediamine (*p*-PHDA), orthophenanthroline (PHEN) and 2,2'-dipyridyl (DIPY), it appears that the ligand is using both

TABLE I. Nickel(II)bis(diphenylphosphorodithioate) Adducts with Diamines.

	Compound[a]	Colour	M.p.	Analysis, found(calcd.)		
				Ni %	P %	N %
I.	$Ni[S_2P(OPh)_2]_2 \cdot$ *p,p'*-DABP	green	189	7.60 (7.30)	7.47 (7.70)	3.22 (3.47)
II.	$Ni[S_2P(OPh)_2]_2 \cdot$ *o,o'*-DABP	green	153	7.39 (7.30)	8.02 (7.70)	3.29 (3.47)
III.	$Ni[S_2P(OPh)_2]_2 \cdot$ 2,7-DAF	green	197	7.04 (7.18)	7.14 (7.59)	3.69 (3.42)
IV.	$Ni[S_2P(OPh)_2]_2 \cdot$ *p*-PHDA	green	172	8.46 (8.05)	8.24 (8.50)	3.62 (3.84)
V.	$Ni[S_2P(OPh)_2]_2 \cdot$ PHEN	green	223	7.59 (7.33)	7.39 (7.98)	3.23 (3.60)
VI.	$Ni[S_2P(OPh)_2]_2 \cdot$ DIPY	green	215	7.68 (7.56)	7.43 (7.98)	3.48 (3.58)
VII.	$Ni[S_2P(OPh)_2]_2 \cdot$ 2 *o*-PHDA	green	163	7.50 (7.19)	7.32 (7.40)	6.48 (6.69)
VIII.	$Ni[S_2P(OPh)_2]_2 \cdot$ 2 *o*-PHDA	pink–purple	170	7.39 (7.19)	7.26 (7.40)	6.39 (6.69)
IX.	$Ni[S_2P(OPh)_2]_2 \cdot$ 3 *o*-PHDA	blue	135	6.37 (6.21)	6.40 (6.56)	8.63 (8.89)
X.	$Ni[S_2P(OPh)_2]_2 \cdot$ 3 PHEN	pink	194	[b]	5.43 (5.32)	7.09 (7.23)
XI.	$Ni[S_2P(OPh)_2]_2 \cdot$ 3 DIPY	pink	187	[b]	5.64 (5.47)	7.59 (7.71)

[a] The following abbreviations were used: DABP, diaminobiphenyl; DAF, diaminofluorene; PHDA, phenylenediamine; DIPY, 2,2'-dipyridyl; PHEN, orthophenanthroline. [b] Nickel could not be determined with dimethylglyoxime from these complexes when the complex was destroyed with HCl or $HNO_3+H_2SO_4$, since it was reformed when ammonia and dimethylglyoxime were added.

its donor nitrogen functions in coordination with the metal. The structure may not be the same, since the ligands with the amino groups in *para* positions cannot coordinate to the same metal atom and the adducts probably have polymeric structure. The *ortho*-diamine and the heterocyclic ditertiary amines (PHEN, DIPY) most probably coordinate to the same nickel atom (as bidentate ligands), as shown before by X-ray crystallography for other adducts of these amines with dialkylphosphorodithioates, *e.g.* $Ni[S_2P(OMe)_2]_2 \cdot PHEN$[8], $Ni[S_2P(OEt)_2]_2 \cdot PHEN$[9] and $Ni[S_2P(OMe)_2]_2 \cdot DIPY$[10].

The 1:2 adducts obtained with *o*-phenylenediamine are the most unusual. As described in the experimental part, two differently coloured isomers were obtained (VII green and VIII pink–purple). This diamine, with the functional groups in *ortho*-position, must be coordinated in the *cis*-positions of the octahedron around the nickel atom. The nature of attachement of the phosphorodithioate ligand will be discussed below in connection with the interpretation of the infrared spectra.

The 1:3 adducts obtained with *o*-PHDA, PHEN and DIPY contain three molecules of the diamine coordinated to nickel, while the phosphorodithioate groups were expelled as free anionic groups (not coordinated to the metal). This is caused by the strong tendency of these diamines to form very stable *cis* complexes and a similar case was previously found for $Ni[S_2P(OMe)_2]_2$ with the same diamines[5].

The adducts prepared in this work are very stable towards dissociation, in marked contrast to many alkylamine adducts of nickel(II)bis(dialkylphosphorodithioates) handled in our laboratory, which often dissociate on evaporation of their solutions with liberation of amine and free nickelbis(dialkylphosphorodithioate).

Electronic Spectra and Magnetic Moments

The electronic spectrum of nickel(II)bis(diphenylphosphorodithioate), not described in the literature, was recorded in *p*-xylene solution. The spectrum contains two bands located in the visible region, which can be assigned to normal transitions of nickel(II) having a D_{4h} configuration:

$$^1A_{1g} \rightarrow {}^1B_{1g} \quad 14.5 \text{ kK}$$
$$^1A_{1g} \rightarrow {}^1B_{2g} \quad 19.0 \text{ kK}$$

The compound is diamagnetic, as expected for a square-planar configuration with a $^1A_{1g}$ ground state of the nickel(II) ion.

The spectra of nickel(II)bis(diphenylphosphorodithioate) amine adducts contain the three bands expected for a (distorted) octahedral (O_h) configuration[11]:

TABLE II. Electronic Spectra and Magnetic Moments of the Adducts.

Compound	Absorption Bands (kK)[a,b]			B (cm^{-1})	β	μ_{eff} (B.M.)
	ν_1	ν_2	ν_3			
I	8.9	14.2	21.0sh (23.6)	740	0.71	3.07
II	10.1	15.4	20.0sh (26.9)	800	0.77	3.11
III	9.0	14.3	22.2sh (22.9)	750	0.72	2.98
IV	9.2	14.9	22.2sh (24.3)	773	0.75	3.01
V	8.9	15.8	22.4	770	0.74	3.14
VI	8.7 9.5	14.8	24.1	780	0.75	3.17
VII	8.5 9.4	15.6	24.4	866	0.84	2.96
VIII	8.3 8.7	18.2	27.9	944	0.91	2.89
IX	11.0 11.9	17.8	27.8	916	0.90	3.08
X	12.8	19.8	–	–	–	2.85
XI	13.1	18.9	–	–	–	2.94

[a] sh = shoulder. [b] The values given in parantheses are the peak positions calculated for the bands showing a shoulder instead of a clear maximum.

ν_1 ($^3A_{2g} \rightarrow {}^3T_{2g}$) ν_2 ($^3A_{2g} \rightarrow {}^3T_{1g}$(F)) and ν_3 ($^3A_{2g} \rightarrow {}^3T_{1g}$(P)). The positions of these bands are listed in Table II, together with the magnetic moments (μ_{eff}).

The spectra are shown in Figure 1 a–c. The spectra of the 1:1 adducts (*e.g.* compounds I, III, and VI in Figure 1a) show the ν_1 bands in the range 8.9–10.1 kK. The bands are not split, thus suggesting the absence of important distorsions of the octahedra. However, some distorsions occuring in compounds VI–VIII result in a splitting of the ν_1 band in two components, separated by 400–900 cm^{-1}. These distorsions may be caused by the closure of a chelate ring with the *cis*-diamines.

The ν_1 band for the compounds containing three molecules of diamine (IX, X and XI) occurs in the order dictated by the spectrochemical series of the ligands. It should be noted that the spectrum of Ni $[S_2P(OPh)_2]_2 \cdot 3o$-PHDA (IX) exhibits absorption bands at the same wavelengths as $NiSO_4 \cdot 3o$-PHDA[12], thus suggesting that the anion does not have any significant influence upon the spectral behaviour of the chromophore. This is the first indication that in compound IX the diphenylphosphorodithioate group occurs as a free anion, rather than a coordinated ligand.

The ν_2 band appears in two different regions of the spectrum: for compounds I–VII in the range 14.2–15.9 kK, and for compounds VIII–XI in the range 17.8–19.8 kK.

The third band, at wavenumbers higher than 20 kK, occurs sometimes as a shoulder, probably masked by a change transfer band expected at wavenumbers

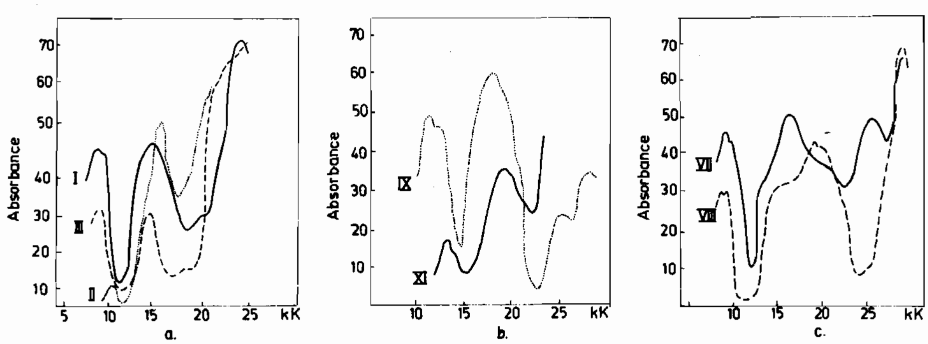

Figure 1. Electronic spectra of the adducts.

higher that 25 kK. For some of the adducts this band is clearly resolved and can be assigned to the ν_3 transition.

The spectra of the two 1:2 isomers, VII and VIII, differ in the position of their absorption maxima (Figure 1c). The occurrence of the ν_1 band at lower wavelengths in the spectrum of the pink–purple isomer (VIII) than in that of the green isomer (VII), suggests a *cis*-structure for the isomer VIII.

The rule of "average environment" was used to determine the value of 10 Dq for $(PhO)_2PS_2^-$ in respect with Ni^{2+} (in a hypothetically six-coordinate complex). The value found was 6972 cm^{-1}, which places the $(PhO)_2PS_2^-$ ligand in the spectrochemical series in the region of strongly covalent bonding ligands.

From the electronic spectral data the Racah parameters B and the covalency factor β were calculated (Table II). The values found are in the same range as for other similar six-coordinate nickel(II) complexes with related ligands.

The magnetic moments (μ_{eff}) are listed in Table II. Their values are, as expected, in the range 2.8–3.2 B.M. These values are close to the spin-only value, suggesting that minimal orbital moment contribution and spin–orbital coupling occur in these six-coordinate nickel(II) compounds with a $^3A_{2g}$ ground term. Similar values were reported in the literature for a number of other nickel(II)bis(dialkylphosphorodithioate)–amine adducts[5].

Infrared Spectra

Vibrational spectra gave useful information concerning the coordinated groups (NH_2 and PS_2). The data are listed in Table III. The presence of two bands in the ν_{NH_2} range (3400–3000 cm^{-1}) indicates the equivalence of the NH_2 groups in respect with the metal in compounds I–IV, *i.e.* the coordination of both NH_2 groups. In compounds I, III and IV, containing the two NH_2 groups in *para* positions, this is possible only with the formation of polymeric structures of type A, shown in Figure 2. In compound II the diamine *o,o'*-DABP apparently forms a seven-membered ring, with the two amino groups occupying a *cis* position in the coordination octahedron (Figure 2, structure B). This type of structure (with *cis* nitrogens) is also expected for compounds V and VI derived from ditertiary heterocyclic amines.

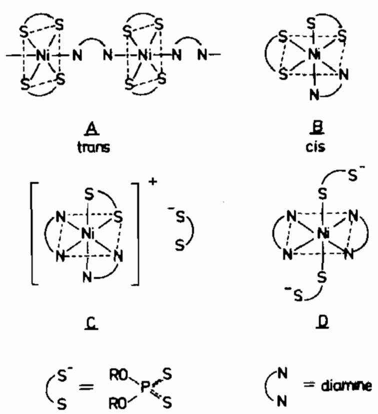

Figure 2. Suggested structures for the adducts.

TABLE III. Infrared Spectral Data (absorption bands in cm^{-1}).

Compound	ν_{NH_2} Bands of the Adduct ν_{as}	ν_{sym}	ν_{NH_2} Bands of the Free Ligand		$\nu_{as}PS_2$	$\nu_{sym}PS_2$	Suggested Type of Coordination of the PS_2 Group
I	3349	3280	3390;	3320	685	590	bidentate
II	3345	3260	3395;	3280	687	590	bidentate
			3380				
III	3350	3280	3380;	3305	690	588	bidentate
IV	3335	3270	3433;	3345	685	589	bidentate
V	–	–	–		691	590	bidentate
					678		
VI	–	–	–		692	590	bidentate
					680		
VII	3330	3270	3400;	3325	690	584	monodentate
	3270	3212			680		
VIII	3220	3180	3400;	3325	695	590	one bidentate
					665	577	and one ionic
IX	3290	3240	3400;	3325	695	587sh	ionic
	3210	3170				577	
X	–	–	–	–	698	590sh	ionic
						580	
XI	–	–	–	–	695	590sh	ionic
						583	

A particular case is that of the isomeric 1:2 adducts obtained with *o*-phenylenediamine (compounds VII and VIII). The data listed in Table III show that all amino groups are coordinated, *i.e.* in both compounds the diamine ligand is bidentate. For the pink–purple adduct VIII the $\nu_{as}NH_2$ band occurs at 3220 cm^{-1}, which represents a shift of *ca.* 180 cm^{-1} relative to the corresponding band of the free amine. Compared to $NiCl_2 \cdot 2$ *o*-PHDA[13] ($\nu_{as}NH_2 = 3205\ cm^{-1}$) the shift is slightly smaller, in accordance with the different strengths of the M–Cl and M–S bonds. In the spectrum of the green adduct there are several νNH_2 bands, the highest energy band being at 3330 cm^{-1}.

The spectrum of compound IX, with three molecules of diamine coordinated to the central Ni(II), exhibits four νNH_2 bands, all at lower wavenumbers than that in the free amine; this large number of bands may be due to some distorsions present in the molecule.

Some information obtained from infrared spectra concerning the interconversion of the isomers VII and VIII should be mentioned here. The green isomer VII obtained directly is identical in the νNH_2 region with the spectrum of the green compound prepared from the pink–purple isomer VIII on heating. The green product obtained from the blue adduct IX exhibits the bands of the free amine, in addition to the bands shifted to 3290, 3240, 3210 and 3170 cm^{-1}; this suggests that the product is a mixture of compound VII with the free amine liberated from the blue adduct IX on heating:

$$\underset{\text{IX}}{[Ni(o\text{-PHDA})_3][S_2P(OPh)_2]_2} \rightarrow \underset{\text{VII (green)}}{[Ni(o\text{-PHDA})_2\{S_2P(OPh)_2\}_2]} + o\text{-PHDA}$$

The PS_2 groups of the diphenylphosphorodithioate ligand are expected to occur at relatively low wavenumbers in the infrared spectrum. Three fundamental vibrations, ν_{as}, ν_{sym} and δ_{PS_2} are to be expected for phosphorodithioates. We could not record the δ_{PS_2} vibration, which occurs at energies lower than 400 cm^{-1}, the limit of our instrument. Therefore, only ν_{as} and ν_{sym} can be considered here.

By comparing the infrared spectrum of $Ni[S_2P(OPh)_2]_2$ (not described in the literature) with the known spectrum of $Ni[S_2P(OEt)_2]_2$, and taking into account the possible effects of the phenyl groups upon the P–S bonds, the bands characteristic for the PS_2 groups can be assigned as $\nu_{as} = 667\ cm^{-1}$ and $\nu_{sym} = 595\ cm^{-1}$ in the planar $Ni[S_2P(OPh)_2]_2$. Compared to Ni(II)bis(diethylphosphorodithioate) the ν_{PS_2} bonds occur at higher wavenumbers; this is explained by the –I and –E effects induced in the molecule by the phenyl groups, compared to the +I effect due to alkyl groups. The electron withdrawing by phenyl groups results in a decreased electron density in the P–S bonds, thus producing a shift towards higher wavenumbers in the diphenylphosphorodithioate group.

The absorption bands observed for ν_{as} and ν_{sym} PS_2, listed in Table III, are shifted in the amine adducts from the values observed for the simple $Ni[S_2P(OPh)_2]_2$ compound.

In the spectra of 1:1 adducts (compounds I–VI) the ν_{as} PS_2 bands are shifted towards higher wavenumbers (shifts up to 20 cm^{-1} are observed), whereas the ν_{sym} PS_2 bands are shifted towards lower wavenumbers (*ca.* 5–7 cm^{-1}), compared to the bands of $Ni[S_2P(OPh)_2]_2$. These shifts are caused by the electronic effects determined by the coordination of the amine.

In the spectra of compounds VII and VIII, containing two amine molecules, a larger number of ν_{PS_2} bands are observed, which can be due to the presence of non-equivalent P–S bonds. The pink–purple adduct VIII exhibits two pairs of bands: one at the same wavenumbers as the adducts with 1:3 ratio (IX–XI, in which the phosphorodithioate group occurs as free anion); the second pair of bands appears at about the same wavenumbers as in $Ni[S_2P(OPh)_2]_2$. On the basis of these facts the pink–purple adduct VIII is tentatively assigned an ionic structure$[NiS_2P(OPh)_2(o\text{-PHDA})_2]^+[S_2P(OPh)_2]^-$ (Figure 2 C), with one bidentate phosphorodithioate group coordinated to the nickel atom, and a free anionic group.

The green isomer VII shows ν_{PS_2} bands close to those observed for the 1:1 adducts. Electronic spectra, as mentioned above, suggest a *trans* structure for this compound, with all amine groups coordinated. This leaves the structure shown in Figure 2 D as the only reasonable possibility, with monodentate phosphorodithioate groups. Such a structure is therefore assigned to compound VII. The occurrence of monodentate phosphorodithioate groups attached to nickel was previously established by X-ray diffraction only in the five-coordinate adduct $Ni[S_2P(OMe)_2]_2 \cdot 2{,}9\text{-}Me_2PHEN$[14], where the second phosphorodithioate group is not coordinated to nickel and occurs as a free anion. Monodentate coordination of $(RO)_2PS_2$ groups can also be inferred for the adduct $Ni[S_2P(OEt)_2]_2 \cdot 4BuNH_2$ reported in the literature[15].

The ν_{PS_2} frequencies observed for compound VII (green) are intermediate between those observed for bidentate and ionic phosphorodithioate groups (Table III). It was shown that for dithiophosphinate ligands the ν_{PS_2} vibrations of R_2PS_2 occur at various wavelengths in the following order[16]: $\nu_{bidentate} < \nu_{monodentate} < \nu_{ionic}$. It is reasonable to assume that a similar regularity holds also for nickel(II)bis(diphenylphosphorodithioate) adducts.

It should be noted that in this case ν_{as} and $\nu_{sym}PS_2$ are shifted in opposite directions, ν_{sym} going towards smaller wavelengths with decreasing denticity of the $(PhO)_2PS_2$ ligand. A possible explanation could reside in the fact that the observed ν_{PS_2} frequencies are combinations of various intramolecular vibrations, rather than pure stretching vibrations as designed. Thus, a normal coordinate analysis[17] of sodium dimethyldithiophosphinate, $Na[S_2PMe_2]$, showed that $\nu_{as}PS_2$ consists of stretchings and contractions of the P–S bonds, whereas ν_{sym} PS_2 is a combination of symmetrical stretchings of P–S and P–C bonds with contractions of the P–C bonds. Thus, the shifts of the corresponding bands are not governed by the same laws as the shifts of ν_{as} PS_2. Depending on the predominance of the stretching or contraction of the P–C bond, ν_{sym} PS_2 can be shifted in one sense or another. Similarly, in the case of diphenylphosphorodithioate, the factors which may influence the shifts of ν_{PS_2} include the multiple contributions to the discussed vibration mode, the electron withdrawing effect and the conjugation effect of the phenyl groups transmitted through the bond system to the P–S bonds. As an overall result there may, therefore, occur a somewhat unusual situation, in which ν_{sym} and ν_{as} PS_2 are shifted in opposite directions.

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