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Vibrational Spectrum, Structure and Complex-Forming Reactions of "Imidobis(diphenylphosphine sulphide)", $(Ph_2PS)_2NH$

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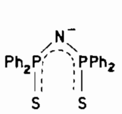
The N–H stretching vibration in $(Ph_2PS)_2NH$, *"imidobis(diphenylphosphine sulphide)" cannot be detected in the i.r. spectrum at room temperature but appears as a very weak band at 3250 cm*$^{-1}$ *at –180 °C. Assignment of an i.r. band at 2640 cm*$^{-1}$ *to an overtone of the N–H bend, rather than an S–H stretch, confirms the imido-structure* $(Ph_2PS)_2NH$ *rather than the thiol structure* $(Ph_2PS)(Ph_2PSH)N$ *for the solid compound. Skeletal* P_2N *stretching vibrations are assigned at 920 and 781 cm*$^{-1}$ *for* $(Ph_2PS)_2NH$ *and at 1199 and 808 cm*$^{-1}$ *for* $[(Ph_2PS)N]^-$. *Reactions of* $(Ph_2PS)_2NH$ *with various transition metal and zinc group acceptors lead ultimately to the formation of products containing the anionic* $[(Ph_2PS)_2N]^-$ *ligand but under very mild conditions complexes containing undissociated* $[(Ph_2PS)_2NH]$ *ligands can be isolated. The ligand field parameters 10 Dq and β are slightly but probably significantly higher for* $Co[(Ph_2PS)_2NH]_2^{2+}$ *than for* $Co[(Ph_2PS)_2N]_2$.

Introduction

*Imidobis(diphenylphosphine sulphide)**, $(Ph_2PS)_2NH$ is a typical example of a group of potential β-difunctional ligands containing no carbon atoms in the chelate ring. A number of complexes of $[(Ph_2PS)_2N]^-$ (I) and related anions have been described in the literature [1–6], but there is little or no information concerning the donor properties or reactivity of the undissociated parent molecule. Schmidpeter and Groeger [7] have examined the i.r. spectrum of solid $(Ph_2PS)_2NH$ and conclude that the molecule has the imido-structure (II) rather than the thiol-structure (III), even though it appears to be necessary to assign a weak band in the usual S–H stretching frequency region (2653 cm^{-1}) [8] to an N–H stretching vibration. We have re-examined the i.r. and Raman spectra of $(Ph_2PS)_2NH$ with the aim of making more positive assignments for the high-frequency and skeletal stretching vibrations, and have also investigated the reactions of $(Ph_2PS)_2NH$ with some representative transition metal and d^{10} acceptor compounds.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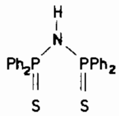
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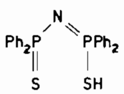
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Experimental

Imidobis(diphenylphosphine sulphide) was obtained commercially (Strem Chemical Inc.) and recrystallised from acetone before use. M.pt. 213 °C [7].

Complexes

$\{CoX_2\cdot(Ph_2PS)_2NH\}$ $(X = Cl, Br, I)$

The hydrated cobalt halide (0.001 mol) was dissolved in boiling acetone and added to a hot solution of the ligand (0.001 mol) in acetone (20 ml). The volume of the solution was reduced on the water bath until crystals began to appear. The blue or green (CoX_2) complexes separated on cooling.

$\{Co[(Ph_2PS)_2NH]_2\}(ClO_4)_2$

This complex was prepared in the same way as the cobalt halide complexes, using a 1:2 metal:ligand ratio and with the addition of ethyl orthoformate to dehydrate the reaction mixture.

$\{Co[(Ph_2PS)_2N]_2\}$

This was obtained by boiling the halide or perchlorate complexes in methanol for a few minutes, or alternatively, separated directly from the reaction of $Co(NO_3)_2\cdot6H_2O$ with $(Ph_2PS)_2NH$ in acetone.

$\{ZnCl_2\cdot(Ph_2PS)_2NH\}$ and $\{HgCl\cdot[(Ph_2PS)_2N]\}$

In each case the metal(II) halide was dissolved in boiling ether and added to an equimolar solution of $(Ph_2PS)_2NH$ in chloroform. The resulting solution was set aside and colourless crystals appeared after about 20 minutes. [The mercury complex is often

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*Commercial name. *Chem. Abs.* entry under "Iminobis-(diphenylphosphine sulphide)" to Vol. 75; 'N-(diphenylphosphinothioyl)-P,P-diphenylphosphinothioic amide' (Vol. 76 on).

analytically slightly impure and may be contaminated with a small amount of $\{HgCl_2 \cdot (Ph_2PS)_2NH]\}$.

$\{Zn[(Ph_2PS)_2N]_2\}$, $\{Cd[(Ph_2PS)_2N]_2\}$ and $\{Hg[(Ph_2PS)_2N]_2\}$

These complexes are the only products when the metal chlorides and $(Ph_2PS)_2NH$ react in acetone solution. The cadmium compound, prepared in ethanol/chloroform solution, rapidly turns yellow, presumably because of decomposition to the sulphide.

$\{CuBr \cdot (Ph_2PS)_2NH\}$

The reaction of $CuBr_2$ in ethanol with an equimolar quantity of $(Ph_2PS)_2NH$ in chloroform yields the copper(I) complex $\{CuBr \cdot (Ph_2PS)_2NH.\}$

$\{Pd[(Ph_2PS)_2N]_2\}$ and $\{Pt[(Ph_2PS)_2N]_2\}$

The reactions of K_2MX_4 (M = Pd, Pt; X = Cl, Br, SCN) with $(Ph_2PS)_2NH$ in acetone or methanol/chloroform solvent systems led to the immediate precipitation of the $\{M[(Ph_2PS)_2N]_2\}$ species.

$\{PdBr_2 \cdot (Ph_2PS)_2NH\}$

This complex was obtained from the reaction of K_2PdBr_4 with $(Ph_2PS)_2NH$ in acetone acidified with about 5% conc. HBr. Similar reactions with K_2PdCl_4, K_2PtCl_4 or K_2PtBr_4, or with $K_2Pd(SCN)_4$ or $K_2Pt(SCN)_4$ in the presence of excess KCNS yield the $\{M[(Ph_2PS)_2N]_2\}$ complexes as the only products.

$[(Ph_2PCl)_2N]Cl$

This was prepared as described by Haubold *et al.* [9].

Spectra

I.r. spectra were obtained using a Perkin–Elmer 457 spectrophotometer. Low temperature spectra of $[(Ph_2PS)_2NH]$ were obtained with a conventional liquid nitrogen cell using a Perkin–Elmer 180 spectrophotometer. Raman spectra were obtained with a Cary 83 Raman spectrophotometer, with 488.0 n.m. laser excitation. Visible spectra were obtained using a Unicam SP700 spectrophotometer.

Discussion

Structure and Vibrational Spectrum of $(Ph_2PS)_2NH$

Vibrational frequency data for $(Ph_2PS)_2NH$ and $[(Ph_2PS)_2N]^-$ [7] over the range 4000–500 cm^{-1} are given in Table II. The assignments for the phenyl group vibrations are made using the original Whiffen [10] notation and follow very closely from those made by Green *et al.* [11, 12, 13] for Ph_3P, Ph_3As and related compounds.

The spectrum of solid $(Ph_2PS)_2NH$ above 2000 cm^{-1} is noteworthy for the absence of any i.r. band or Raman line which can readily be assigned to the N–H stretching vibration. In the closely related molecule $(Ph_2P)_2NH$ the N–H stretching mode gives rise to a well-defined i.r. band at 3215 cm^{-1} [14, 15], but solid $(Ph_2PS)_2NH$ exhibits no detectable i.r. absorption or Raman shift above the C–H stretching band at 3060 cm^{-1}. Schmidpeter and Groeger [7] assign weak i.r. bands at 2967 cm^{-1} and 2653 cm^{-1} to 'P_2NH group' vibrations, presumably with predominant N–H stretching character, and base their proposed imido-structure for $(Ph_2PS)_2NH$ mainly on comparisons of the low-frequency skeletal vibrations with those in related molecules and ions. In our spectra, apart from the C–H stretching band {identified by comparison with $[(Ph_2PS)N]^-$ and $(Ph_2PS)_2CH_2$} we observe a medium–weak i.r. band and Raman line at 2640 cm^{-1} and another very weak Raman line at 2560 cm^{-1}. We have been unable to

TABLE I. Analytical Data for New Complexes.

Complex	C		H		S		Halogen		N	
	Found	Calc	Found	Calc	Found	Calc	Found	Calc	Found	Calc
$\{CoCl_2[(Ph_2PS)_2NH]\}$	49.7	49.7	3.8	3.6	10.9	11.1	12.3	12.2	–	–
$\{CoBr_2[(Ph_2PS)_2NH]\}$	42.8	43.1	3.4	3.2	9.6	9.6	23.3	23.9	–	–
$\{CoI_2[(Ph_2PS)_2NH]\}$	37.5	37.8	3.3	2.8	8.7	8.4	33.2	33.3	–	–
$\{Co[(Ph_2PS)_2NH]_2\}(ClO_4)_2$	49.9	49.8	4.1	3.7	–	–	5.7	6.1	2.6	2.4
$\{ZnCl_2[(Ph_2PS)_2NH]\}^a$	–	–	–	–	10.7	10.9	11.7	12.1	–	–
$\{CuBr[(Ph_2PS)_2NH]\}$	47.9	48.6	4.2	3.6	11.3	10.8	12.7	13.5	–	–
$\{PdBr_2[(Ph_2PS)_2NH]\}$	40.9	40.3	3.3	3.0	9.1	9.0	–	–	–	–
$\{Pd[(Ph_2PS)_2N]_2\}$	57.2	57.5	3.9	4.0	13.1	12.8	–	–	2.6	2.8
$\{Pt[(Ph_2PS)_2N]_2\}$	52.8	52.8	3.8	3.7	11.9	11.7	–	–	–	–
$\{HgCl[(Ph_2PS)_2N]\}$	40.5	42.1	3.3	2.9	9.6	9.4	5.6	5.2	2.2	2.1
$\{Hg[(Ph_2PS)_2N]_2\}$	52.4	52.5	4.1	3.7	11.9	11.7	–	–	–	–

^{a}Unstable complex.

TABLE II. Vibrational Spectra of $(Ph_2PS)_2NH$ and $[(Ph_2PS)_2N]^-$.

Assignment[a]	$(Ph_2PS)_2NH$		$[(Ph_2PS)_2N]^-$
	I.R., cm^{-1} [b]	Raman, Δν, cm^{-1} [c]	I.R., cm^{-1} [b,d]
νN–H	3250, w, br[e,f]		
νC–H	3060, w	3048, m	3054, w
	2967, w?[d]		
2 × 1326	2640, mw[g,h]	2638, w	
		2560, vw	
νC–C(k)	1585, w	1586, ms	1585, w
νC–C(l)	1575, vw	1578, m	
νC–C(m)		1475, vw	1476, w
νC–C(n)	1440, s		
	1435, s	1436, w	1438, s
δN–H	1326, ms[i]	1329, w	
νC–C(o)?	1305, m	1306, w	1302, w
			1293, w
βC–H(e)	1280, w	1280, vvw	1279, w
νP$_2$N			1199, vs
βC–H(a)	1178, mw	1179, m	1171, s
βC–H(c)	1160, w	1162, m	1156, m
		1155, sh	
X-sens(q)	1108, sh	1105, s	1112, sh
	1105, s		1099, s
βC–H(d)	1070, m	1070, w	1067, w
βC–H(b)	1025, sh, w	1027, ms	1027, m
	1020, w		
Ring (p)	995, w	1000, vs	999, w
γC–H(h)	970, vw	970, w	986, w
			983, w
γC–H(i)			921, w
νP$_2$N	935, m	935, w	
	922, vs	920, w, br	
	919, vs		
γC–H(g)	853, w	851, w	865, w
	846, vw		850, w
νP$_2$N	781, s	782, w	808, s
γC–H(f)	750, ms	754, w	750, s
	738, s	747, w	740, m
X-sens(r)	719, s	719, m	713, s
	714, s	710, mw	701, vs
φC–C(v)	685, s		693, s
			688, s
			662, w
νP–S antisym	645, s	645, mw	
νP–S sym	622, w	625, vs	
αC–C–C(s)	611, mw	614, vs	614, m
νP–S			598, s
			576, s
	570, w	*570, vw*	
X-sens(y)	530, m	532, w	
+	500, s	500, sh	511, s
skeletal?	492, m	492, w	

[a] Internal phenyl-group vibrations are labelled in conformity with refs. [10–13]. Frequencies italicised are not assigned. [b] Nujol mulls. [c] Powder. [d] See ref. [7]. [e] At –180 °C. [f] 3326 cm^{-1} in $CHCl_3$ solution. [g] 2688 cm^{-1} in $CHCl_3$ solution. [h] 2649 cm^{-1} at –180 °C. [i] 1330 cm^{-1} at –180 °C.

v, very; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

identify positively the weak i.r. band reported at 2967 cm^{-1} by Schmidpeter and Groeger: a number of samples do absorb in this region but the bands are very sensitive to impurity and virtually disappear after several recrystallisations.

The appearance of an i.r. band and Raman line at 2640 cm^{-1} at first sight suggests an S–H rather than an N–H stretching vibration [8]. Examination of the spectra in the N–H bending frequency region, however, reveals a medium-intensity i.r. band at 1326 cm^{-1} in $(Ph_2PS)_2NH$, with no counterpart in $[(Ph_2PS)_2N]^-$, which we assign to the N–H bending mode [7]. The frequency of the 2640 cm^{-1} band is thus appropriate for the first overtone of the bending vibration. At liquid nitrogen temperature the 1326 cm^{-1} band shifts to 1330 cm^{-1} and the 2640 cm^{-1} band shifts to 2649 cm^{-1}, the intensity remaining about the same as in the spectrum at ambient temperature. The respective shifts of these bands are consistent with their assignment to the fundamental and overtone of the N–H bending mode. Also, if the 2640 band were to arise from an N–H stretching fundamental a significant increase in intensity and sharpening might be expected upon cooling. At the same time, in the low-temperature spectrum, a weak broad absorption appears in the N–H stretching region at 3250 cm^{-1}.

The N–H vibrations in solid $(Ph_2PS)_2NH$, unlike those in $(Ph_2P)_2NH$ [14, 15], are clearly very much affected by intermolecular (and possibly intramolecular) hydrogen-bonding interactions. In solution this problem does not arise and the N–H stretch gives rise to a strong sharp i.r. band at 3326 cm^{-1} ($CHCl_3$). Significantly, the bending overtone continues to appear in the solution spectrum, at 2688 cm^{-1}; there can be no question here of its assignment to an N–H or S–H stretching vibration.

The assignments for the principal skeletal stretching modes in $(Ph_2PS)_2NH$ are relatively straightforward. The P–C stretches contribute [11–13] to the so-called 'X-sensitive' modes and are not separately identifiable. In general, the X-sensitive bands show only minor variations between $(Ph_2PS)_2NH$ and $[(Ph_2PS)_2N]^-$. The P–N stretching vibrations in $(Ph_2PS)_2NH$ occur at 922 cm^{-1} and 781 cm^{-1}, within the normal frequency range for single-bonded P–N stretching modes [16, 17]. In $[(Ph_2PS)_2N]^-$ the higher-frequency band appears at 1199 cm^{-1}, in the usual P=N stretching region, but the lower band moves only slightly, to 808 cm^{-1}. Corresponding pairs of bands occur at 898 and 800 cm^{-1}, approx., in $(Ph_2P)_2NH$ [14] and at 1233 and 795 cm^{-1} in $[(Ph_2PCl)_2N]^+$, but are missing in $(Ph_2PS)_2CH_2$, Ph_2PPPh_2, $Ph_2P(S)P(S)Ph_2$ [18] or Ph_3PS. The assignment of the band near 800 cm^{-1} to a vibration with predominant P–N stretching character therefore appears to be justified despite its relative insensitivity to changes in P–N bond order.

Phosphorus–sulphur stretching vibrations in phosphine sulphides usually occur between 550–650 cm^{-1} [18]. Schmidpeter and Groeger [7] mention i.r. bands at 652 cm^{-1} (s) and 615 cm (vw) in $(Ph_2PS)_2NH$ but in our spectra we find three vibrations in this region, at 645 cm^{-1} (i.r., s; R, w), 622 cm^{-1} (i.r., m; R, vs) and 611 cm^{-1} (i.r., m; R, s). The band at 611 cm^{-1} also appears in $[(Ph_2PS)_2N]^-$; we therefore assign it to the 's' fundamental of the phenyl ring. The relative i.r. and Raman intensities of the bands at 645 cm^{-1} and 622 cm^{-1} then lead to their assignment to the antisymmetric and symmetric P–S stretching modes, respectively.

The P–S stretching vibrations in $[(Ph_2PS)_2N]^-$ occur at significantly lower frequencies than those in $(Ph_2PS)_2NH$, giving rise to strong i.r. bands at 598 cm^{-1} and 570 cm^{-1}. The frequency shifts are consistent with a decrease in P–S bond order associated with the formation of the $[(Ph_2PS)_2N]^-$ ion (I).

Complex-forming Reactions

As a general rule, reactions of $(Ph_2PS)_2NH$ with transition metal or d^{10} metal acceptors lead to the formation of compounds of the type $\{M[(Ph_2PS)_2N]_n\}$, containing the $[(Ph_2PS)_2N]^-$ ion, as the final product. Davison and Switkes [2] have prepared a number of these compounds from the potassium salt $K[(Ph_2PS)_2N]$ but in our experience reactions with $(Ph_2PS)_2NH$ in methanol or ethanol solution proceed directly in very good yield and the initial preparation of the alkali metal salt is unnecessary. Greater difficulties arise in the preparation of complexes containing the undissociated $(Ph_2PS)_2NH$ ligand. Under suitably mild conditions we have been able to isolate complexes of $(Ph_2PS)_2NH$ with cobalt halides, cobalt perchlorate, zinc chloride and copper(I) bromide. Where the acceptor atoms have more pronounced class 'b' [19] character, however, isolation of $(Ph_2PS)_2NH$ complexes is very much more difficult. Reactions with palladium(II) and platinum(II) chloride, bromide or thiocyanate yielded only one $(Ph_2PS)_2NH$ complex, with $PdBr_2$. With the other palladium and platinum compounds, even when relatively large amounts of acid were added in an attempt to suppress dissociation of the ligand molecule, only the $[(Ph_2PS)_2N]^-$ complexes $\{M[(Ph_2PS)_2N]_2\}$ were obtained. Mercury(II) chloride reacts with $(Ph_2PS)_2NH$ in ether/chloroform to form $\{HgCl[(Ph_2PS)_2N]\}$; the corresponding reaction in methanol proceeds directly to $\{Hg[(Ph_2PS)_2N]_2\}$. All of the $(Ph_2PS)_2NH$ complexes are quantitatively converted to the corresponding $[(Ph_2PS)_2N]^-$ compounds by boiling for a few minutes in methanol.

Details of the more important vibrational frequencies in the $(Ph_2PS)_2NH$ and $[(Ph_2PS)_2N]^-$ complexes are given in Table III. The two types of complexes are readily distinguished by the position of the higher-frequency P_2N stretching band, which appears near

TABLE III. Vibrational Spectra of $[(Ph_2PS)_2NH]$ and $[(Ph_2PS)_2N]^-$ Complexes (I.R. frequencies, cm^{-1}, Nujol Mulls).

	νN–H	νP$_2$N			νP–S		νM–L[a]		
$[(Ph_2PS)_2NH]$	3400 vvw		935 m 922 vs 919 vs	781 s	645 s[b]	622 w[c]			
$\{CoCl_2[(Ph_2PS)_2NH]\}$	3400 vvw, br		920 s	798 s	605 ms	589 s	327 m,	310 s,	286 m[d]
$\{CoBr_2[(Ph_2PS)_2NH]\}$	3400 vvw, br		932 m, sh 920 s	792 s 781 s	600 m	588 s	290 m		
$\{CoI_2[(Ph_2PS)_2NH]\}$	3400 vvw, br		931 s 920 sh	788 s	601 m	588 s	285 mw		
$\{Co[(Ph_2PS)_2NH]_2\}(ClO_4)_2$[e]	3450 w, br		920 s	800 s	600 m	592 s	330 m,	313 s,	287 m
$\{CuBr[(Ph_2PS)_2NH]\}$	3340 w, br		910 s	809 ms	621 s[f] 609 ms	599 s			
$\{ZnCl_2[(Ph_2PS)_2NH]\}$	3420 vw, br		921 s	800 s	602 ms	595 s	315 sh,	300 ms,	280 sh[d]
$\{PdBr_2[(Ph_2PS)_2NH]\}$			899 s	818 m	600 m	592 s	310 m		
$[Ph_2PS)_2N]^-$		1199 vs		808 s	598 s	576 s			
$\{Co[(Ph_2PS)_2N]_2\}$		1210 s		810 m 798 s	582 ms	568 vs	300 w,	285 m	
$\{Pd[(Ph_2PS)_2N]_2\}$		1180 m, sh 1160 s, br[g]		822 s	578 s	570 s	330m?,	295 ms,	280 sh
$\{Pt[(Ph_2PS)_2N]_2\}$		1210 m, sh 1180 m, sh 1160 s, br[g]		830 m, sh 820 s	575 s, sh	569 vs	310m?		
$\{Cd[(Ph_2PS)_2N_2\}$		1240 s 1210 s, br		795 m, sh 786 s	585 s	565 s	270 ms		
$\{HgCl[(Ph_2PS)N]\}$		1240 m, sh 1220 s, br 1160 m, br[g]		781 m	565 sh	560 s	284 vs[h]		
$Hg[(Ph_2PS)N]_2$		1240 s 1220 s		795 m, sh 787 s	586 m 580 m	565 s			

[a] Tentative assignments. Weak ligand bands also appear near 300 cm^{-1}. [b] Antisymmetric. [c] Symmetric. [d] νM–Cl + νM–S. [e] 'Ionic perchlorate' bands at 1100 cm^{-1}, s, br, 621 cm^{-1}, m. [f] One of these bands presumably arises from the 's' phenyl ring vibration. [g] Overlaps with strong phenyl-group absorptions near 1170–1160 cm^{-1}. [h] νHg–Cl.

TABLE IV. Visible Spectra and Ligand Field Parameters for Tetrahedral Cobalt Complexes of $(Ph_2PS)_2NH$, $[(Ph_2PS)_2N]^-$ and Some Related Ligands.

	ν_3 (cm^{-1})	$\bar{\nu}_3$ (cm^{-1})	ν_2 (cm^{-1})	$\bar{\nu}_2$ (cm^{-1})	10Dq (cm^{-1})	B (cm^{-1})	β^c	Ref.
$\{Co[(Ph_2PS)_2NH]_2\}(ClO_4)_2$[a]	15000 13950 12600	15200	7300	7300	4210	635	0.65	
$\{CoCl_2[(Ph_2PS)_2NH]\}$[b]	16450 14900 13300	14650	6400 6000	6250	3660	665	0.68	
$\{CoBr_2[(Ph_2PS)_2NH]\}$[b]	16500 14200 13350	14900	6600	6600	3830	662	0.68	
$\{CoI_2[(Ph_2PS)_2NH]\}$[b]	14950 12900	13720	6400	6400	3580	595	0.61	
$\{Co[(Ph_2PS)_2N]_2\}$		14258		6613	4027	586	0.60	[2]
$\{Co[(Ph_2PS)_2CH_2]_2\}(ClO_4)_2$		14460		6655	3900		0.65	[20]
$\{Co[(NH_2)_2CS]_2\}(ClO_4)_2$		14500		7200	4250	600	0.62	[21]

[a] In $EtNO_2$. [b] Nujol mulls. [c] B for gaseous $Co^{2+} = 976$ cm^{-1}.

1200 cm^{-1} in the $[(Ph_2PS)_2N]^-$ compounds but falls to about 900 cm^{-1} in the $(Ph_2PS)_2NH$ compounds. The P–S stretching frequencies in $(Ph_2PS)_2NH$ fall by 30–60 cm^{-1} on coordination, the antisymmetric mode being the more sensitive, but the corresponding shifts in $[(Ph_2PS)_2N]^-$ are considerably smaller (10–30 cm^{-1}). In most of the $(Ph_2PS)_2NH$ complexes a very weak broad band appears in the N–H stretching region around 3300–3400 cm^{-1}: there are no corresponding bands in the $[(Ph_2PS)_2N]^-$ complexes.

Details of the visible spectra of the cobalt complexes, and the ligand field parameters 10Dq and β calculated from them, are listed in Table IV. The values of 10Dq and β are appreciably higher for $\{Co[(Ph_2PS)_2NH]_2\}^{2+}$ than for $\{Co[(Ph_2PS)_2N]_2\}$: the differences between the two sets of values are rather too large to arise simply from uncertainties in estimating the centres of the ν_2 and ν_3 absorption bands. If we accept that the P$\overset{\cdots}{-}$S bond order in $[(Ph_2PS)_2N]^-$ will be lower than that in $(Ph_2PS)_2NH$, it follows that the sulphur atoms in $[(Ph_2PS)_2N]^-$ will be more polarisable than those in $(Ph_2PS)_2NH$ and hence that $[(Ph_2PS)_2N]^-$ will have the lower β value. The values of 10Dq and β for $(Ph_2PS)_2NH$ are close to those exhibited by related monodentate and bidentate neutral S-donor ligands $(NH_2)_2CS$, [20] and $(Ph_2PS)_2CH_2$ [21]

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