

Vibrational and NMR spectroscopic studies of cadmium(II) bis(dialkyl dithiophosphinates)

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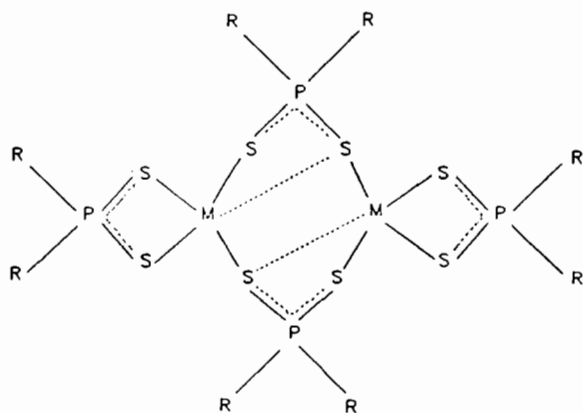
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Abstract

The compounds $[\text{Cd}(\text{S}_2\text{PR}_2)_2]$ (R = ethyl and cyclohexyl) have been studied in the solid state by vibrational (IR and Raman) spectroscopy and in solution in CH_2Cl_2 using molecular weight measurements and IR and NMR (^{13}C , ^{31}P , ^{113}Cd) spectroscopy. The influence of tributylphosphine on the association of the compounds in solution and on the coordination of the metallic centre has been explored.

Introduction

Bis(diethyldithiophosphinato)cadmium(II) $[\text{Cd}(\text{S}_2\text{PEt}_2)_2]$ was first prepared by Malatesta and Pizzotti by reacting the ammonium salt of diethyldithiophosphinic acid with cadmium sulfate [1]. Later, Kuchen *et al.* extended this work using new synthetic procedures [2]. Recently, Wunderlich [3] and Svensson and Albertsson [4] determined the structure of $[\text{Cd}(\text{S}_2\text{PEt}_2)_2]$ from single-crystal X-ray diffraction data. The compound is a dimer formed about a crystallographic centre of symmetry in an arrangement similar to those observed in cadmium(II) and zinc(II) iso-propyldithiophosphates and some zinc(II) and manganese(II) dithiophosphinates [5].



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In $[\text{Cd}(\text{S}_2\text{P}(\text{O}^i\text{Pr})_2)_2]$, the Cd...S distances of 3.194(8) Å [5a] across the central eight-membered ring of the dimer (dotted lines in the figure), though long for Cd–S coordination, are shorter than the sum of the van der Waals radii (3.40 Å) [6]. The presence of these weak interactions suggests that some residual Lewis acidity remains on the metallic centre after formation of the four principal Cd–S bonds. Indeed, several derivatives of bis(dialkyldithiophosphato)cadmium(II) with anionic or neutral Lewis bases have been isolated, some of which have been studied by X-ray diffraction [7, 8]. Results have also been published concerning cadmium(II) dithiophosphates and their adducts in low coordinating solvents [9].

According to our calculations using published positional parameters [3, 4], Cd...S distances in $[\text{Cd}(\text{S}_2\text{PEt}_2)_2]$ are *c.* 3.1 Å, suggesting the presence of weak Cd...S interactions and some residual Lewis acidity on the metal. Further information on cadmium(II) dithiophosphinates in solution and their possible interaction with Lewis bases is scarce. Molecular weight measurements suggest that some dimer–monomer equilibrium occurs [2], and a polarographic investigation in ethanol–water solutions indicated that bis(diethyldithiophosphinato)cadmium(II) is more stable than the diethyldithiophosphate and diethyldithiophosphonate analogues [10].

We report here the results of a comparative vibrational and NMR study of $[\text{Cd}(\text{S}_2\text{PEt}_2)_2]$ and bis(dicyclohexyldithiophosphinato)cadmium(II), $[\text{Cd}(\text{S}_2\text{PCy}_2)_2]$,

and of an exploration of the systems $[\text{Cd}(\text{S}_2\text{PR}_2)_2]/$ tributylphosphine (PBu_3) in dichloromethane solution.

Experimental

Materials and instrumentation

$\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Merck) and dicyclohexyldithiophosphinic acid (Strem) were used as received. Sodium diethyldithiophosphinate dihydrate ($\text{NaS}_2\text{PEt}_2 \cdot 2\text{H}_2\text{O}$) was prepared by published methods [11]. Tetraethylammonium dicyclohexyldithiophosphinate was obtained by addition of a solution of HS_2PCy_2 (1.55 g, 5.89 mmol) in chloroform/acetone (c. 20 ml) to a solution of tetraethylammonium hydroxide (0.86 g, 5.89 mmol) in water (c. 30 ml) obtained by treatment of tetraethylammonium bromide with a freshly prepared aqueous suspension of Ag_2O . Diethyldithiophosphinic acid for NMR measurements was obtained *in situ* as described before for $\text{HS}_2\text{P}(\text{OEt})_2$ [12]. Elemental analyses were performed with a Carlo Erba 1108 microanalyser. Mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS90 data system and operating under EI conditions (direct insertion probe, 70 eV, 250 °C). All the ions mentioned below were identified by use of DS90 software. IR spectra were recorded in KBr pellets or CH_2Cl_2 solution on an FT-IR Mattson Cygnus 100 spectrometer, and Raman spectra were obtained with a Dilor Omars 89 spectrometer (argon ion laser, 5145 Å). X-ray diffraction measurements were performed at room temperature using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation. Cell parameters were determined by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $9 < \theta < 17^\circ$; $\lambda = 0.71073$ Å. Molecular weights were measured in chloroform with a Knauer vapour-pressure osmometer. Proton decoupled ^{13}C (62.83 MHz), ^{31}P (101.26 MHz) and ^{113}Cd (55.84 MHz) NMR spectra were recorded in CDCl_3 or $\text{DMSO}-d_6$ (in 5 or 10 mm o.d. tubes at room temperature) on a Bruker WM-250 spectrometer and were referred to the solvent signal, 85% H_3PO_4 and 0.1 M $\text{Cd}(\text{ClO}_4)_2$, respectively.

Preparation of $[\text{Cd}(\text{S}_2\text{PEt}_2)_2]$

By a slight modification of procedure 3 of Kuchen *et al.* [2a] $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was reacted with $\text{NaS}_2\text{PEt}_2 \cdot 2\text{H}_2\text{O}$ (1:2 mol ratio) in ethanol. The white solid formed after stirring was filtered out, washed with ethanol and dried under vacuum. M.p. 165 °C. *Anal.* Found: C, 23.5; H, 5.7; S, 31.0. Calc. for $\text{C}_8\text{H}_{20}\text{P}_2\text{S}_4\text{Cd}$: C, 22.9; H, 4.8; S, 30.6%. Molar conductivity: 7.3 $\text{S cm}^2 \text{mol}^{-1}$ (10^{-3} M in DMSO). The base peak and main metallated ions in the mass spectrum (based on the isotope ^{114}Cd) were at m/z (%) = 153 (R_2PS_2 , 100),

420 (M , 64), 392 ($M\text{-R} + \text{H}$, 34), 363 ($M\text{-2R} + \text{H}$, 32), 331 ($M\text{-S-2R} + \text{H}$, 5), 267 ($M\text{-(S}_2\text{PR}_2) + \text{H}$, 52). Monocrystals were grown overnight after storage of the mother liquid in a refrigerator. Crystal data: orthorhombic, space group $Pbca$, $a = 12.040(1)$, $b = 13.789(3)$, $c = 20.278(2)$ Å, $U = 3367(1)$ Å³, $Z = 8$, $D_c = 1.653$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 19.325$ cm^{-1} .

Preparation of $[\text{Cd}(\text{S}_2\text{PCy}_2)_2]$

$\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.56 g, 1.33 mmol) dissolved in ethanol (10 ml) was slowly added, with stirring, to HS_2PCy_2 (0.70 g, 2.66 mmol) in ethanol (70 ml). The white precipitate formed after stirring overnight was isolated, washed with ethanol and dried under vacuum. M.p. 220 °C. *Anal.* Found: C, 45.8; H, 7.6; S, 20.5. Calc. for $\text{C}_{48}\text{H}_{44}\text{P}_2\text{S}_4\text{Cd}$: C, 45.4; H, 7.0; S, 20.2%. Molar conductivity: 4.1 $\text{S cm}^2 \text{mol}^{-1}$ (10^{-3} M in DMSO). The base peak and main metallated ions in the mass spectrum were at m/z (%) = 83 (R , 100), 554 ($M\text{-R} + \text{H}$, 9), 471 ($M\text{-2R} + \text{H}$, 5).

Results and discussion

Identification of the compounds

The analytical data are in keeping with the expected $[\text{Cd}(\text{S}_2\text{PR}_2)_2]$ stoichiometry. The mass spectral data of the ethyl derivative are in general agreement with those reported by Heinz *et al.* [13]. Though no signals for dimeric species were detected, the crystallographic data (see 'Experimental') clearly indicate that we isolated the same dimeric compound as was studied before [3, 4]. $[\text{Cd}(\text{S}_2\text{PCy}_2)_2]$ proved to be rather unstable under electron impact, and only very weak peaks for metallated species could be observed.

IR and Raman solid state spectra

Table 1 lists the most significant bands for the salts of the ligands and the compounds prepared. For the diethyldithiophosphinate ligand, the spectra of its sodium salt and the cadmium complex all show a strong IR band around 600 cm^{-1} and a medium-strong band (strong in Raman) around 500 cm^{-1} which are attributed to $\nu_{\text{asym}}(\text{PS})$ and $\nu_{\text{sym}}(\text{PS})$, respectively. For other dithiophosphinates the interval between the positions of these bands, $\Delta\nu$, has been used as an indication of the coordination mode of the ligand, since it appears to be sensitive to whether there are two equivalent $\text{P}=\text{S}$ bonds (when the ligand is bidentate) or non-equivalent $\text{P}=\text{S}$ and $\text{P}-\text{S}$ bonds (in monodentate dithiophosphinates) [16, 17], even when the $\text{P}-\text{S}$ distance is rather insensitive [18, 19]. In studies of diethyldithiophosphinates, however, neither the $\text{P}-\text{S}$ distances nor $\Delta\nu$ have proved sensitive to the ligand coordination mode (Table 2). In keeping with this, we found for

TABLE 1. IR and Raman data^a

Compound	$\nu_{\text{asym}}(\text{PS})$		$\nu_{\text{sym}}(\text{PS})$		$\Delta\nu$	Experimental conditions
	IR	R	IR	R		
NaS ₂ PEt ₂ ·2H ₂ O	619vs		511m	512vs	108	solid state
MeS ₂ PEt ₂ ^b	585		477		108	solid state
(S ₂ PEt ₂) ₂ ^c	576		471 ^d		105	solid state
[Cd(S ₂ PEt ₂) ₂]	600vs		486s	486vs	114	solid state
	606m		484m		118	in CH ₂ Cl ₂ solution
Cd(S ₂ PEt ₂) ₂ + PBu ₃	606m		484m		121	in CH ₂ Cl ₂ solution
Cd(S ₂ PEt ₂) ₂ + 2PBu ₃	606m		484m		121	in CH ₂ Cl ₂ solution
HS ₂ PCy ₂	632vs		522s	525m	110	solid state
[Et ₄ N][S ₂ PCy ₂]	623vs		550s	550m	73	solid state
[Cd(S ₂ PCy ₂) ₂]	606vs		550s	548s	56	solid state
	608m		548m		60	in CH ₂ Cl ₂ solution
Cd(S ₂ PCy ₂) ₂ + PBu ₃	615m		550m		65	in CH ₂ Cl ₂ solution
Cd(S ₂ PCy ₂) ₂ + 2PBu ₃	615m		550m		65	in CH ₂ Cl ₂ solution

^am = medium; s = strong; vs = very strong. ^bData from ref. 14. ^cData from ref. 15. ^dAverage of splitted bands.

TABLE 2. X-ray and IR data for the sodium salt and complexes of S₂PEt₂

	[SnMe ₂ (S ₂ PEt ₂) ₂]	NaS ₂ PEt ₂ ·2H ₂ O	[Cd(S ₂ PEt ₂) ₂]		[Pb(S ₂ PEt ₂) ₂]	[Zn(S ₂ PEt ₂) ₂]	
Coordination type ^a	M		BR	A	A	BR	BI
P-S(1)	2.054(2)	2.034(2)	2.030(3)	2.031(3)	2.036(8)	2.060(10)	2.057(15)
P-S(2)	1.961(2)	1.993(2)	2.028(3)	1.991(3)	1.931(10)	1.990(9)	1.999(12)
Δ	0.093	0.041	0.012	0.040	0.105 ^b	0.070 ^b	0.058 ^b
Reference	14	20		4	4		5b
$\nu_{\text{asym}}(\text{P-S})$	590	619, 616	595 ^c	600	595 ^c		595 ^c
$\nu_{\text{sym}}(\text{P-S})$	473	511, 512	488	486	495 ^c		488
$\Delta\nu$	117	108, 104	107	114	100		107
Reference	14	this work, 15	15	this work	15		15

^aM = monodentate; BI = bidentate; BR = bridge; A = anisobidentate. ^bMaximum value in the crystallographic ligands slightly different. ^cAverage of splitted bands.

[Cd(S₂PEt₂)₂] a value of $\Delta\nu$ (114 cm⁻¹) close to the 117 cm⁻¹ found for [SnMe₂(S₂PEt₂)₂] (in which X-ray data showed the ligand to be monodentate [14]), even though the crystallographic data (ref. 4, this work) show the presence of both bridging and slightly anisobidentate chelating ligands. Furthermore, the value of $\Delta\nu$ in the cadmium compound is also similar to those found in the sodium salt, Et₂P(S)SMe and Et₂P(S)S-S(S)PEt₂ (Table 1), even though the two PS bonds in the latter two compounds must be essentially P-S and P=S. We conclude that $\Delta\nu$ is not sensitive enough to the ligand bonding scheme to be useful for identification of the ligand coordination mode in diethyldithiophosphinate compounds.

For dicyclohexyldithiophosphinates the situation seems to be different. The values of $\Delta\nu$ for the tetraethylammonium salt and the dithioacid (Table 1) clearly show sensitivity to the rearrangement of the PS₂ moiety. The value obtained for [Cd(S₂PCy₂)₂] sug-

gests the presence of bidentate chelate and/or bridging ligands.

Behaviour in solution

Measurement of molecular weight in CHCl₃ solution (Table 3) showed that, like the diethyl derivative [2] and dithiophosphate compounds [9, 21, 22], both dithiophosphinates are associated in this medium. For the cyclohexyl derivative, the data suggest equilibrium between monomeric and dimeric species. The values for [Cd(S₂PEt₂)₂] suggest the involvement of higher oligomers.

The ³¹P NMR spectra, like those of dithiophosphate compounds [9, 21], consisted of a single resonance (Table 4), showing that the lability of the compounds afforded a time-averaged spectrum. The phosphorus nuclide is heavily deshielded by coordination to cadmium, probably because the inductive effect of the metal predominates over the other complex factors that contribute to ³¹P chemical shifts [23]. The ¹³C NMR

TABLE 3. Calculated and observed molecular weight of cadmium complexes in chloroform solution

Compound	Molality ($\times 10^{-3}$)	Molecular weight		
		Calculated	Experimental	n^a
[Cd(S ₂ PEt ₂) ₂]	13.9	418.86	933.45	2.2
	16.2		991.03	2.4
[Cd(S ₂ PEt ₂) ₂] + PBu ₃	16.8	621.18	519.59	0.8
[Cd(S ₂ PCy ₂) ₂]	15.1	635.22	976.95	1.5
	14.9		962.67	1.5
[Cd(S ₂ PCy ₂) ₂] + PBu ₃	4.3	837.54	545.58	0.7

^aMolecular weight found/formula weight.

TABLE 4. Significant NMR parameters

Compound	$\delta(^{13}\text{C})$	$^1J(^{13}\text{C}-^{31}\text{P})$	$\delta(^{31}\text{P})$	$\delta(^{113}\text{Cd})$
HS ₂ PEt ₂	31.65d ^a	52.2	73.4s	
[Cd(S ₂ PEt ₂) ₂]	31.77d	48.2	81.6s	407.9s
			89.3s ^b	213.3s ^b
HS ₂ PCy ₂	41.82d	46.7	85.9s	
[Cd(S ₂ PCy ₂) ₂]	42.08d	42.9	93.0s	402.8s
			83.3s ^b	254.8s ^b

^ad = doublet, s = singlet. ^bIn DMSO-d₆ as solvent.

signals are at only slightly higher frequencies in the cadmium compounds than in the free acid, but the $^1J(^{13}\text{C}-^{31}\text{P})$ coupling constants clearly decrease upon coordination. The cadmium signal is at lower frequency than in cadmium(II) dithiophosphates [9]; this was expected, since in view of the inductive effect of R and RO groups [24] the donor capacity of dithiophosphinates should be greater than that of dithiophosphates (and the stability constant β_2 of [Cd(S₂PEt₂)₂] is in fact greater than that of [Cd{S₂P(OEt)₂}₂] [10]). The $\delta(^{113}\text{Cd})$ values in DMSO solution are little more than half those recorded in chloroform, suggesting that DMSO coordinates to the cadmium, but since no significant degree of ionization occurs (see conductivity values in 'Experimental'), the DMSO does not completely displace the dithiophosphinate ligand. Both the introduction of the oxygen atoms in the cadmium coordination sphere and the possible increase of the coordination number at the metallic centre should result in more shielded values of $\delta(^{113}\text{Cd})$ [25].

Reaction with neutral donors was further explored, only in solution, using a more moderate Lewis base/cadmium dithiophosphinate ratio (Table 5). Tributylphosphine (PBu₃) was selected as the Lewis base in order to facilitate comparison with the results obtained by Bond *et al.* [9] with cadmium dithiophosphates and this phosphine. As in the latter experiments, the ³¹P NMR spectrum of a 1:1 stoichiometric mixture of [Cd(S₂PEt₂)₂] and PBu₃ showed two signals; the coupling

of the phosphine resonance with the metal was not observable at room temperature, but on cooling satellite signals appeared on either side of the phosphine resonance (Fig. 1(a)) and the single signal in the cadmium spectrum split into a doublet (Fig. 1(c)). As in the case of dithiophosphates [9], these results indicate that the ligand exchange equilibrium, which at room temperature is fast on the NMR time-scale for both the dithiophosphinato and phosphine ligands, first becomes relatively slow for PBu₃ as temperature decreases. Coupling between the phosphine and the metal is observable at a higher temperature in [Cd(S₂PEt₂)₂] than in cadmium dithiophosphates [9].

Molecular weight measurements (Table 3) indicate that, in the presence of phosphine, the dimeric nature of [Cd(S₂PEt₂)₂] is practically lost, so that the bridging ligands become chelating. At the same time, the observed effect of DMSO is in keeping with the suggestion of Bond *et al.* [9] (for [Cd{S₂P(OEt)₂}]) that, probably, PBu₃ displaces one sulfur of an Et₂PS₂⁻ ligand that becomes monodentate. Note that the more pronounced anisobidentate nature of the dithiophosphinate [4, 5a] probably allows easier evolution toward monodenticity. With this picture of the 1:1 adduct, the coordination number of cadmium remains basically four (allowing for partial phosphine dissociation), the initial [CdS₄] kernel of the monomer changing to [CdS₃P]. The small change in $\delta(^{113}\text{Cd})$ for [Cd(S₂PEt₂)₂] + PBu₃ (Fig. 1(c)) in relation to [Cd(S₂PEt₂)₂] (Table 4) is also in keeping with this hypothesis.

TABLE 5. NMR data for $[\text{Cd}(\text{S}_2\text{PR}_2)_2] + n\text{PBu}_3$ mixtures in CD_2Cl_2 solution

Compound	$\delta(^{31}\text{P})$		$^1J(^{31}\text{P}-^{113}\text{Cd})$	$\delta(^{113}\text{Cd})$	T (K)	[M]
	S_2PR_2	PBu_3				
$[\text{Cd}(\text{S}_2\text{PEt}_2)_2]$	83.3s			412.9s	293	≈ 0.50
$[\text{Cd}(\text{S}_2\text{PEt}_2)_2] + \text{PBu}_3^a$	81.8s	-15.2	1802	425.7d	253	
$[\text{Cd}(\text{S}_2\text{PEt}_2)_2] + 2\text{PBu}_3$	77.0s	-14.6	1507	546.2t	183	
$[\text{Cd}(\text{S}_2\text{PCy}_2)_2]$	95.7s			407.2s	293	≈ 0.02
$[\text{Cd}(\text{S}_2\text{PCy}_2)_2] + \text{PBu}_3$	92.7t	-17.5	1764	427.4d ^b	233	
$[\text{Cd}(\text{S}_2\text{PCy}_2)_2] + 2\text{PBu}_3$	92.9s	-17.7 -32.4	1741	430.1d	185	

^aAt 243 K both $^1J(^{31}\text{P}-^{111}\text{Cd}) = 1803.5$ Hz and $^1J(^{31}\text{P}-^{113}\text{Cd}) = 1885.7$ Hz can be observed. ^b T (K) = 213.

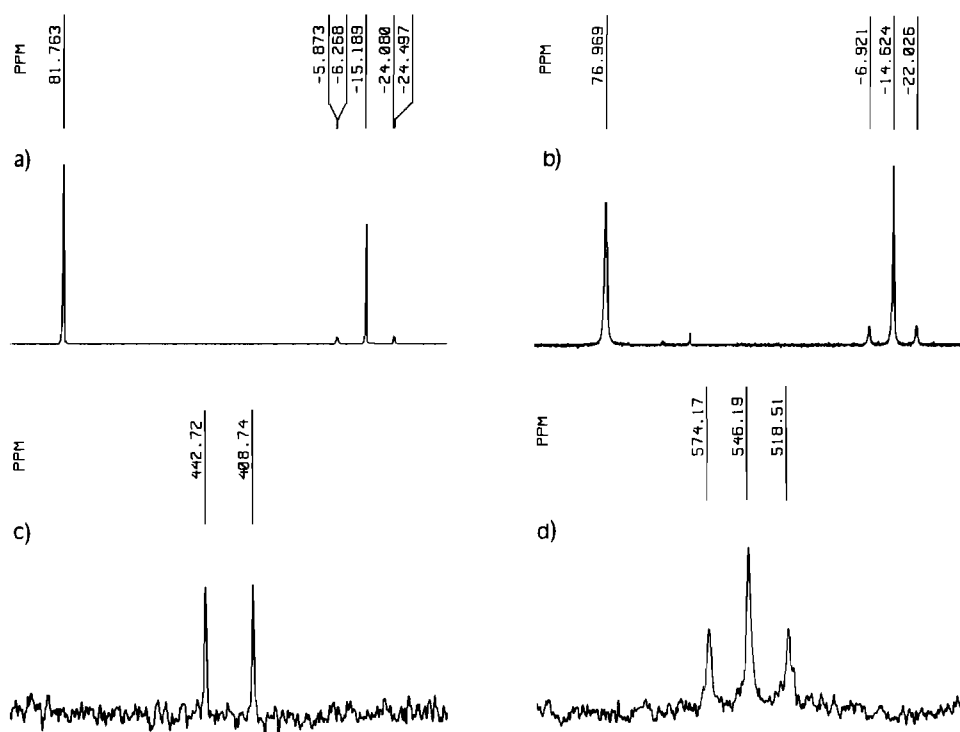


Fig. 1. ^{31}P (a, b) and ^{113}Cd (c, d) NMR spectra of $[\text{Cd}(\text{S}_2\text{PET}_2)_2] + n\text{PBu}_3$ mixtures in CD_2Cl_2 . (a) $n=1$ at 243 K; (b) $n=2$ at 183 K; (c) $n=1$ at 243 K; (d) $n=2$ at 183 K.

For the 1:2 adduct the experimental behaviour is also very similar to that of dithiophosphate compounds [9]. In fact, the temperature at which the coupling between cadmium and phosphine becomes observable is practically the same. The structure of the compound present is nevertheless an open question. In the solid state, bis(*O,O'*-diethyldithiophosphato)bis(hexamethylenetetramine)cadmium(II) has two chelated dithio ligands forming the equatorial plane and the two amine ligands occupying the apical positions of a pseudo-octahedral arrangement around the cadmium atom [8]. The large shift in $\delta(^{113}\text{Cd})$ for $[\text{Cd}(\text{S}_2\text{PET}_2)_2] + 2\text{PBu}_3$ suggests that in this compound too the coordination scheme must differ significantly from that of the 1:1

adduct. However, although a structure similar to that of the hexamethylenetetramine adduct would increase the coordination number and therefore the shielding of the cadmium nuclide, it would also introduce two additional deshielding atoms (an S and a P) in the coordination sphere of the metal, making the chemical shift difficult to predict *a priori*.

The NMR behaviour of $[\text{Cd}(\text{S}_2\text{PCy}_2)_2]$ in presence of PBu_3 is, in general, similar to that described for $[\text{Cd}(\text{S}_2\text{PET}_2)_2]$ except for the 1:2 stoichiometric mixture. In this mixture one mole of phosphine remains uncoordinated showing that only the 1:1 adduct is formed. This difference may be due to the greater steric hindrance of the cyclohexyl groups preventing the second

molecule of PBu_3 from coordinating to the metallic centre.

The IR spectra in solution show broad bands for $\nu_{\text{asym}}(\text{P-S})$ and $\nu_{\text{sym}}(\text{P-S})$ in positions close to those found for both complexes in the solid state (Table 1). The broadening of the bands is in keeping with the coexistence of several species in solution due to associative and/or dissociative equilibria. Upon addition of phosphine, $\Delta\nu$ slightly increases, as is expected if the dithiophosphinate ligand partially evolves toward monodentate behaviour.

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