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Preparation and Single-Crystal Characterization of ^{i}Pr$_2$P(S)NHP(S)^{i}Pr$_2$ and Homoleptic [^{i}Pr$_2$P(S)NP(S)^{i}Pr$_2$]$^-$ Complexes of Zinc, Cadmium, and Nickel

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There have been a substantial number of studies[1−8] into the coordination chemistry of Ph$_2$P(S)NHP(S)Ph$_2$ since this type of ligand is readily prepared and provides an inorganic analog of β-diketonates. There is rather less work on alkyl analogs R$_2$P(S)NHP(S)R$_2$ although some studies on methyl complexes have been reported.[9−12] We and others have recently noted the remarkable conformational differences that are possible for MS$_2$P$_2$N rings.[13,14] Furthermore, the report[15] on the structure of Me$_2$P(S)NHP(S)Me$_2$ and that of Co{S$_2$PMe$_2$)N}$_2$ prompts us to report on investigations into the synthesis and coordination chemistry of HN(^{iso}Pr$_2$PS)$_2$. Here we describe the synthesis and X-ray structure of the neutral ligand as well as complexes of the formula [M{N(^{iso}Pr$_2$PS)$_2$}$_2$] (M = Zn (**1**), Cd (**2**), Ni (**3**)). **1** and **2** were characterized by ^{31}P NMR, FTIR, FTR, FAB$^+$ mass spectroscopy, microanalyses and X-ray crystallography. **3** was characterized by FTIR, FAB$^+$ mass spectroscopy, microanalyses, and X-ray crystallography. The structures of **1**−**3** all reveal isostructural tetrahedral complexes of the anionic ligand.

Experimental Section

FT infrared spectra were recorded on a Perkin-Elmer 1720X FT spectrometer, Raman spectra were recorded on a Perkin-Elmer 1700X FT spectrometer with a Systems Nd/YAG laser (1064 nm), NMR spectra were recorded on a JEOL JNM EX270 MHZ spectrometer, mass spectra were recorded on a VG Autospec Q, and microanalyses were performed by the microanalytical service of Imperial College.

^{i}Pr$_2$P(S)NHP(S)^{i}Pr$_2$. This method is based on a literature preparation of related compounds,[16] and the reaction was performed under nitrogen. A solution of ^{i}Pr$_2$PCl (4.87 g, 32 mmol) in toluene (100 mL) was added dropwise to a solution of HN(SiMe$_3$)$_2$ (2.58 g, 16.0 mmol) in hot (50 °C) toluene (50 mL) over 30 min. Heating and stirring was continued for 3 h after which time the reaction was cooled to room temperature and sulfur was added (1.0 g, 31 mmol). The reaction was then refluxed for a further 6 h and cooled to 0 °C. The resulting white precipitate was filtered off and washed with CS$_2$ (2 × 10 mL) and light petroleum ether (2 × 10 mL). The crude product was recrystallized from CH$_2$Cl$_2$/hexane to give 2.90 g, 58% yield of the pure compound. Mp: 165−166 °C. Anal. Calcd for C$_{12}$H$_{29}$NP$_2$S$_2$: C, 46.0; H, 9.3; N, 4.4; S, 20.5; P, 19.8. Found: C, 45.9; H, 8.5; N, 4.5; S, 20.4; P, 20.9. ^{31}P{^{1}H} NMR (CDCl$_3$): 91.2 ppm. MS: m/z = 314 and 627 corresponding to [M + H]$^+$ and [M$_2$ + H]$^+$ were observed with the expected isotopic distribution patterns.

Zn[N(^{iso}Pr$_2$PS)$_2$]$_2$, 1. ZnCO$_3$·2Zn(OH)$_2$.H$_2$O (0.10 g, 0.29 mmol) was added to a solution of HN(^{iso}Pr$_2$PS)$_2$ (0.30 g, 0.96 mmol) in dichloromethane (30 mL), and the mixture was refluxed for 2 h. The cloudy/white mixture was filtered and the filtrate was reduced by two-thirds and cooled overnight to give the product as clear crystals, yield 90%. Mp: 144 °C. Anal. Calcd for C$_{24}$H$_{56}$N$_2$P$_4$S$_4$Zn: C, 41.9; H, 8.2; N, 4.1; S, 18.6; P, 18.0. Found: C, 42.6; H, 7.4; N, 4.4; S, 18.6; P, 18.7. ^{31}P{^{1}H} NMR (CDCl$_3$) 64.43 ppm. FAB$^+$ MS: m/z 689 [corresponds to [Zn{N(^{iso}Pr$_2$PS)$_2$}$_2$ + H$^+$].

{**Cd[N(^{iso}Pr$_2$PS)$_2$]$_2$**}**, 2.** CdCO$_3$ (0.10 g, 0.58 mmol) was added to a solution of HN(^{iso}Pr$_2$PS)$_2$ (0.363 g, 1.16 mmol) in dichloromethane (30 mL), and the mixture was refluxed for 2 h. Again the mixture was cloudy white, and it was filtered, the filtrate being evaporated to dryness as a white solid. Then colourless crystals were obtained from dichloromethane/petroleum ether (40−60 °C), yield 86%. Mp: 161 °C. Anal. Calcd for C$_{24}$H$_{56}$N$_2$P$_4$S$_4$Cd: C, 39.2; H, 7.7; N, 3.8; S, 17.4; P, 16.9. Found: C, 38.7; H, 6.5; N, 3.8; S, 17.0; P, 18.0. ^{31}P{^{1}H} NMR (CDCl$_3$): 63.09 ppm. FAB$^+$ MS: m/z 739 [corresponds to [Cd{N(^{iso}Pr$_2$PS)$_2$}$_2$ + H$^+$].

{**Ni[N(^{iso}Pr$_2$PS)$_2$]$_2$**}**, 3.** 2NiCO$_3$·3Ni(OH)$_2$·4H$_2$O (0.10 g, 0.17 mmol) was added to a solution of HN(^{iso}Pr$_2$PS)$_2$ (0.16 g, 0.51 mmol) in dichloromethane (30 mL), and the green mixture was refluxed for 2 h. The green filtrate was evaporated to a green solid, then green crystals were obtained from dichloromethane/petroleum ether (40−60 °C), yield 83%. Mp: 126 °C. Anal. Calcd for C$_{24}$H$_{56}$N$_2$ P$_4$S$_4$Ni: C, 42.3; H, 8.3; N, 4.1; S, 18.8; P, 18.2. Found: C, 42.6; H, 7.9; N, 4.1; S, 18.7; P, 19.3. FAB$^+$ MS: m/z 683 [corresponds to [Ni{N(^{iso}Pr$_2$PS)$_2$}$_2$ + H$^+$].

Crystallography. Details of the data collections and refinements are summarized in Table 1. The structure of **LH** was determined independently at IC and LU and details of the experimental data are included for comparision only. Data were collected using $\omega/2\theta$ scans (Rigaku AFC7S diffractometer at LUT) or ω scans (Siemens diffractometer at IC). Intensities were corrected for Lorentz−polarisation and as indicated in Table 1 for absorption. The structures were solved by direct methods except for **3** which was solved by the heavy atom method. In all cases all of the non-hydrogen atoms were refined anisotropically, in **LH** the position of the N−H proton was located from a ΔF map. The positions of the remaining hydrogens were idealized. Refinements were by full-matrix least squares based on F using either SHELXTL[17] or teXsan.[18] The complete listing of the crystal data is provided in the Supporting Information.

Results and Discussion

The synthesis of ^{i}Pr$_2$P(S)^{i}Pr$_2$ (**LH**) proceeded smoothly using the method previously reported for related systems.[16]

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Table 1

	LH[a]	**1**	**2**	**3**
empirical formula	$C_{12}H_{29}NP_2S_2$	$C_{24}H_{56}N_2P_4S_4Zn$	$C_{24}H_{56}CdN_2P_4S_4$	$C_{24}H_{56}N_2N_iP_4S_4$
space group	$P2_1/a$	$I4_1/a$(No 88)	$P\bar{1}$	$I4_1/a$
diffractometer	Rigaku AFC7S [Siemens P4/PC]	Siemens P4/PC	Siemens P4/PC	Rigaku AFC7S
radiation	Cu Kα [Mo Kα]	Cu Kα	Mo Kα	Cu Kα
unit cell dimensions				
a (Å)	12.000(3) [12.013(13)]	15.928(2)	9.288(6)	15.845(1)
b (Å)	10.506(2) [10.497(5)]		12.929(8)	
c (Å)	14.556(2) [14.569(13)]	13.941(2)	16.452(10)	13.974(3)
α (deg)			78.97(5)	
β (deg)	105.45(1) [105.44(7)]		77.83(5)	
γ (deg)			69.46(5)	
volume (Å$^{3)}$	1770 [1771]	3537	1794	3509
Z	4	4	2	4
fw	313.4	690.2	737.2	683.5
final R, R_w	3.6, 3.6 [4.04, 4.28]	3.98, 4.82	3.05, 3.46	3.70, 3.80

[a] Two independent data collections; parameters which were different in the data collection performed at IC are in square brackets.

Table 2. Selected IR and Raman Data for **LH** and **1**−**3** (cm^{-1})

	ν(PNP)		*ν*(PS)		
compound	IR	R	IR	R	*ν*(MS) R
LH[a]	936	944	646	656	
1	1226	1165	563/541	566	279
2	1230	1160	548		256
3	1225		558		258

[a] *ν*(NH) 3243, *δ*(NH) 1322 cm^{-1}.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **LH** and **1**−**3**

	LH	M = Zn (**1**)	M = Cd (**2**)	M = Ni (**3**)
P(1)−S(1)	1.941(1)	2.032(1)	2.018(2)	2.027(1)
P(2)−S(2)	1.949(1)		2.032(2)	
P(3)−S(3)			2.023(2)	
P(4)−S(4)			2.022(2)	
P(1)−N(1)	1.682(3)	1.581(2)	1.585(3)	1.581(2)
P(2)−N(1)	1.684(2)		1.580(3)	
P(3)−N(3)			1.573(3)	
P(4)−N(3)			1.592(3)	
M−S(1)		2.345(1)	2.526(2)	2.2844(9)
M−S(2)			2.516(2)	
M−S(3)			2.531(2)	
M−S(4)			2.514(2)	
S(1)−P(1)−N(1)	114.14(9)	118.5(1)	119.0(1)	118.0(1)
S(2)−P(2)−N(1)	114.76(10)		118.5(1)	
S(3)−P(3)−N(3)			119.2(1)	
S(4)−P(4)−N(3)			119.2(1)	
P(1)−N(1)−P(2)	131.6(1)	140.5(3)	143.2(2)	137.1(2)
P(3)−N(3)−P(4)			141.0(2)	
M−S(1)−P(1)		107.1(1)	103.4(1)	111.00(4)
M−S(2)−P(2)			103.8(1)	
M−S(3)−P(3)			104.2(1)	
M−S(4)−P(4)			103.8(1)	
S(1)−M−S(2)		112.4(1)	110.6(1)	109.86(2)
S(3)−M−S(4)			109.4(1)	
S(1)M−S(4)		108.0(1)	108.1(1)	108.69(4)
S(2)−M−S(3)			107.3(1)	
S(1)−M−S(3)			111.8(1)	
S(2)−M−S(4)			109.5(1)	

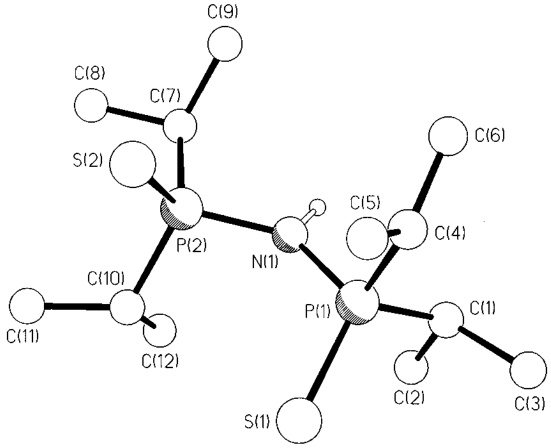

Figure 1. X-ray structure of $^{i}Pr_2P(S)NHP(S)^{i}Pr_2$.

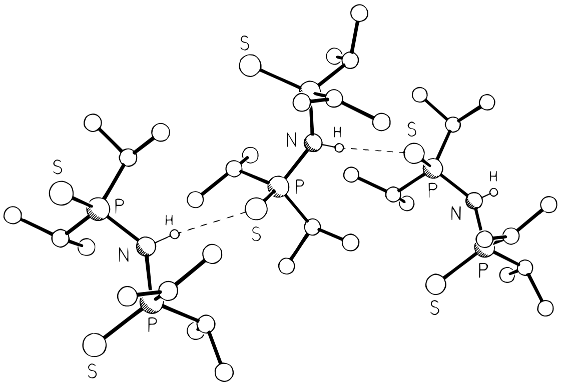

Figure 2. Part of the H-bonded chain in the structure of $^{i}Pr_2P(S)$-$NHP(S)^{i}Pr_2$.

Reaction of **LH** with metal carbonates gave **1**−**3** in good yields. All of the compounds gave satisfactory elemental analyses and display the expected spectroscopic properties. FAB mass spectra revealed the expected parent ions. Deprotonation/complexation of **LH** to give **1** and **2** resulted in a coordination shift of the phosphorus nuclei of approximately 30 ppm. Furthermore, as has been observed in related systems[19,20] there is a marked increase in the frequency of the *ν*(PNP) vibration of **1**−**3** compared to the free ligand.

The structure of **LH** (Figure 1) adopts a different conformation to that of the phenyl[5,21,22] and methyl[15] analogs both of which have *anti* conformations of the sulfur atoms. The isopropyl compound reported here has a *gauche* arrangement of the sulfur atoms with the S−P···P−S 'torsion angle' being 79°; P(1)−S(1) and P(2)−S(2) are rotated by 36° and 43° (in opposite directions) with respect to the P−N−P plane. The geometries about each phosphorus center are essentially the same; there are noticeable distortions from tetrahedral with a slight enlargement of the S−P−C angle and a marked asym-

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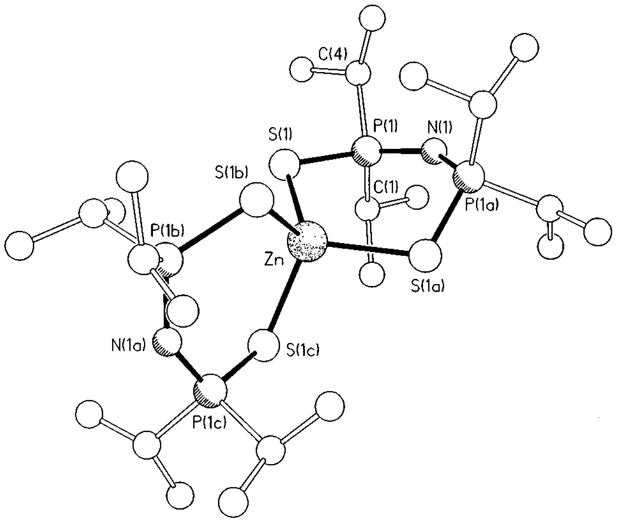

Figure 3. X-ray structure of **1**. **3** is isomorphous and is not illustrated.

metry in the N$-$P$-$(S/^{i}Pr) angles with the N$-$P$-$C angles being contracted and the N$-$P$-$S angles being enlarged from ideal tetrahedral. The angle at nitrogen [131.6(1)°] is enlarged somewhat from trigonal but comparable to that observed in the methyl and phenyl analogs. The P$-$N bond lengths are equivalent and are similar to those reported for related systems. The molecules in **LH** pack (Figure 2) to form H-bonded chains that extend in the crystallographic *a* direction [S(2)$\cdots$N 3.57 Å, S(2)$\cdots$H 2.60 Å, S$\cdots$H$-$N 170°]. This arrangement, which is similar to the methyl analog[15] is in contrast to the phenyl analog[5,21,22] which is known to form dimer pairs. Although the difference in P$=$S bond lengths is small [1.949(1) cf. 1.941(1) Å] and at the margin of significance the longer bond is associated with the H-bonded sulfur atom.

Complexation/deprotonation of **LH** gives tetrahedral ML_2 complexes (M = Zn **1**, Cd **2**, Ni **3**) which are essentially isostructural—indeed the zinc and nickel compounds are isomorphous. The zinc complex **1** has crystallographic S_4 symmetry, the Zn$-$S distance being 2.345(1) Å. The S$-$Zn$-$S bite angle is 112.4(1)° and the other S$-$Zn$-$S angle is 108.0(1)°. The ZnS_2P_2N rings have puckered geometries with a pseudoboat conformation. This conformation appears to be the most commonly adopted for complexes containing $[R_2P(S)NP(S)R_2]^-$ ligands although other conformations have been reported.[13,14] The P$-$S bond lengths in **1** are enlarged and the P$-$N bond lengths reduced with respect to **LH** reflecting the increased electronic delocalization as a consequence of deprotonation. The distortions in the geometries at phosphorus that were observed in the free ligand [angles ranging from 101 to 115°] are also present in **1** with angles in the range 104.9(1)$-$118.5(1)°; the largest distortions are associated with N$-$P$-$S in both cases. On complexation the P$-$N$-$P angle is substantially increased [140.5(3) in **1** *vs* 131.6(1)° in **LH**] which is in striking contrast to the change in geometry upon complexation to cobalt for the methyl analog[15] [128.0(3)° $Co\{S_2PMe_2)N\}_2$ *vs* 133.2(2)° for $Me_2P(S)NHP(S)Me_2$]. The reasons for this difference are not immediately apparent and cannot be attributed simply to steric interactions associated with the ^{i}Pr substituents. As mentioned above, **1**$-$**3** are essentially isostructural, with **1** and **3** being isomorphous. A least-squares fit of the core atoms in **1** and **2** reveals only very minor differences. Inspection of the packing of the three complexes does not reveal any significant intermolecular approaches to either the sulfur or nitrogen atoms.

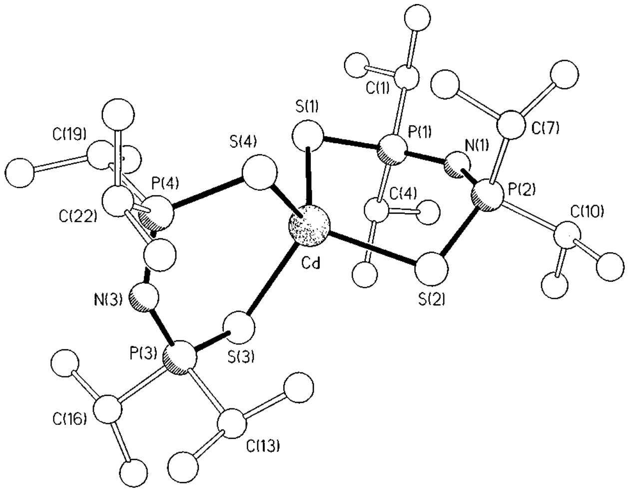

Figure 4. X-ray structure of **2**.

Supporting Information Available: Text describing the experimental crystallographic structure determination for **HL** and 3 tables giving experimental crystallographic details, bond lengths, bond angles, torsion angles and anisotropic displacement parameters for non-hydrogen atoms and atomic coordinates for hydrogen atoms for **HL** (two independent data collections), **1**, **2** and **3**, and ORTEP drawings of **HL**, **1**, and **2** (60 pages). Ordering information is given on any current masthead page.

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