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Synthesis and single crystal structure of a three coordinate complex of mercury(II) with 1-(ethylthio)-2-(diphenylphosphino) ethane (L) prepared by a new simple method

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Abstract

The (P, S) ligand 1-(ethylthio)-2-(diphenylphosphino) ethane (L) is synthesized by reacting Ph₂PLi with CH₃CH₂SCH₂CH₂Cl. The yield is good (~85%) and the method of preparation is simpler than the liquid ammonia based one reported earlier. Its complexation with Cu(I), Hg(II) and organometallic species of Ru(II) are explored. All the complexes and the ligand exhibit characteristic proton, carbon-13 and phosphorus-31 NMR spectra. The single crystal structure of the Hg(II) complex has been determined. It is found to be a three coordinate complex. The sum of the bond angles at Hg, viz. P(1)–Hg(1)–Br(1), P(1)–Hg(1)–Br(2) and Br(1)–Hg(1)–Br(2), is $\approx 360^{\circ}$. Thus the geometry around Hg can best be described as essentially trigonal planar. The Hg(1)–P(1) bond length is 2.415(1) Å and the Hg–Br bond lengths are 2.5152(6) and 2.5952(6) Å. There exists a weak secondary interaction between Hg and the S donor site of the ligand [Hg(1)···S(1) bond distance 3.063(1) Å < sum of van der Waal's radii 3.35 Å]. © 2006 Elsevier Ltd. All rights reserved.

Keywords: 1-(Ethylthio)-2-(diphenylphosphino) ethane; Copper; Ruthenium; Mercury; Complex; Three coordinate complex; Single crystal structure

1. Introduction

Hybrid phosphine ligands containing a sulfur donor atom, viz. 1-(alkyl/arylthio)-2-(diphenylphosphino) ethane, have been synthesized by reacting sodium diphenylphosphide with the appropriate organic halide in liquid ammonia, and their metal complexes with Ni(0), Rh(I), Ir(I), (CO)₂Co(I), Pt(II), (η^3 -2-Me-allyl)Pd(II), Co(II), Ru(II) and Co(III) have been explored [1–10]. A sister ligand, Ph₂PCH₂SCH₃, and its complexes with Pd(II), Pt(II) and Rh(I) have also been explored [11,12]. We have found that 1-(ethylthio)-2-(diphenylphosphino) ethane (L) is obtained easily (yield ~ 85%) when PPh₂Li reacts with $C_2H_5SCH_2CH_2Cl$ in THF at -78 °C. This also avoids the handling of obnoxious liquid ammonia.

$$\mathsf{PPh}_2\mathsf{Cl} + \mathsf{Li} \xrightarrow{\mathsf{THF}} \mathsf{PPh}_2\mathsf{Li} + \mathsf{CH}_3\mathsf{CH}_2\mathsf{SCH}_2\mathsf{CH}_2\mathsf{CI} \xrightarrow{\mathsf{THF}} \mathsf{PPh}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_2\mathsf{CH}_3$$

The reactions of L with Cu_2Br_2 , $HgBr_2$ and [Ru(p-cym $ene)Cl_2]$ have not been previously studied, and therefore they are investigated in detail and the results are reported in the present paper. Single crystals of $[HgBr_2(L)]$ (2) were found to be suitable for X-ray diffraction and therefore its single crystal structure was determined. Mercury in this complex is three coordinated as L coordinates through phosphorus only. The distance between Hg and sulfur is long but less than the sum of the van der Waal's radii, indicating a weak interaction only. The proton and carbon-13 NMR of L and all its metal complexes are characteristic. The long Hg–S bond (weak interaction) is a surprising

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result, as the biological chemistry of mercury is dominated by coordination to cysteine [13]. The preference of Hg for sulfur donor sites, due to its soft nature, is well known. In mercury thiolates, apart from the Hg–S bond, the possibility of a secondary mercury(II)–sulfur interaction has also been reported [14–16], which makes it difficult to anticipate the structures of such complexes.

2. Experimental

The C and H analyses were carried out with a Perkin-Elmer elemental analyzer 240 C. The ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13 and 75.47 MHz, respectively. ${}^{31}P{}^{\bar{1}}H{}$ NMR spectra were recorded at 121.49 MHz using H₃PO₄ as an external indicator. IR spectra in the range 4000-250 cm⁻¹ were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. The conductance measurements were made in acetonitrile (concentration $\sim 1 \text{ mM}$) using an ORION conductivity meter model 162. The molecular weights (concentration \sim 5 mM) in chloroform were determined with a Knauer vapour pressure osmometer model A0280. The melting points determined in open capillary are reported as such. The Ph₂PCl and 2-chloroethyl ethyl sulfide were obtained from Aldrich (USA). [RuCl₂(*p*-cymene)]₂ was synthesized by the reported method [17].

2.1. Synthesis of 1-(ethylthio)-2-(diphenylphosphino) ethane (L)

Chlorodiphenylphosphine solution $(5.0 \text{ cm}^3 \text{ of } 1.0 \text{ M})$ solution in THF) was added to lithium (0.63 g, 5.0 mmol) in dry THF (25 cm³) at room temperature in a Schlenk flask. The mixture was stirred until the solution became dark red in colour, which indicated the formation of lithium diphenylphosphide. The PPh₂Li was then filtered and transferred to a Schlenk tube under nitrogen atmosphere and cooled to -78 °C. 2-Chloroethyl ethyl sulfide (0.62 g, 5.0 mmol) was added to it with constant stirring. The mixture was allowed to come to room temperature over ~ 12 h, after which all the THF was evaporated off from the mixture on a rotary evaporator and the residue was dissolved in deoxygenated dichloromethane (30 cm^3) . The solution was again concentrated to $\sim 10 \text{ cm}^3$ on a rotary evaporator and mixed with hexane (30 cm³). The resulting solid was then recrystallized with a dichloromethane-methanol mixture (1:1) to obtain L as a white crystalline solid. Yield ~85%; m.p. 45 °C. Anal. Calc.: C, 70.04, H, 6.98. Found: C, 70.01; H, 6.30%. ¹H NMR (δ vs TMS, CDCl₃, 25 °C): 1.17-1.22 (t, 3H, H₁), 2.30-2.35 (m, 2H, H₄), 2.49-2.62 (m, 4H, H₃ and H₂), 7.32–7.47 (m, 10H, Ar-H of PPh₂).

2.2. Synthesis of $[CuBr(L)]_2(1)$

To a solution of L (0.13 g, 0.50 mmol) made in 10 cm³ of chloroform was added Cu₂Br₂ (0.07 g, 0.50 mmol) dis-

solved in 10 cm³ of nitromethane under nitrogen atmosphere. The resulting mixture was stirred under an inert nitrogen atmosphere for 2 h at room temperature. Thereafter, the solution was filtered through celite. The clear filtrate was concentrated to $\sim 10 \text{ cm}^3$ on a rotary evaporator and mixed with hexane (20 cm^3) . The resulting white solid was filtered, washed with hexane $(3 \times 20 \text{ cm}^3)$ and dried in vacuo and stored under inert conditions. Complex 1 was recrystallized from chloroform-hexane mixture (1:1). Yield: 75%; m.p.: 78 °C (d). Anal. Calc.: C, 38.79, H, 3.81. Found: C, 38.72, H, 3.01%. $\Lambda_{\rm m}$: 6.50 Ω^{-1} cm² mol⁻¹; ¹H NMR (δ vs TMS, CDCl₃, 25 °C) 1.21–1.26 (t, 3H, H₁), 2.58-2.60 (m, 2H, H₄), 2.69-2.76 (m, 2H, H₂), 2.83-2.88 $(m, 2H, H_3)$, 7.30–7.47 $(m, 10H, Ar-H of -PPh_2)$; ¹³C{¹H} NMR (δ vs TMS, 25 °C), 13.5 (C₁), 26.5, 26.7 (C₄), 29.5, 29.7 (C₂), 30.1 (C₃), 128.7, 128.8, 130.8, 131.2, 132.5, 133.1, 133.3 (Ar-C of PPh₂).

2.3. Synthesis of $[HgBr_2(L)]$ (2)

HgBr₂ (0.20 g, 0.55 mmol) was dissolved in acetone (20 cm^3) and mixed with a solution of L (0.15 g)0.55 mmol) in chloroform (20 cm³). The resulting mixture was stirred at room temperature until the ligand L was consumed (as monitored by TLC). The solvent was removed from the mixture on a rotary evaporator. The resulting residue was dissolved in 20 cm³ of chloroform and filtered through celite. The filtrate was concentrated to 10 cm^3 on a rotary evaporator and mixed with 20 cm³ of hexane. The white complex 2 was filtered, dried in vacuo and recrystallized from chloroform-hexane (1:1) mixture. Yield: 80%; m.p.: 135 °C. Anal. Calc.: C, 30.26, H, 2.29. Found: C, 30.04, H, 2.66%. Molecular weight; found: 659.0, calculated: 634.39; $\Lambda_{\rm m}$: 4.60 Ω^{-1} cm² mol⁻¹; ¹H NMR (δ vs TMS, CDCl₃, 25 °C), 1.27-1.32 (t, 3H, H₁), 2.66-3.11 (m, 6H, H₄, H₃ and H₂), 7.59-7.80 (m, 10H, Ar-H of $-PPh_2$); ${}^{13}C{}^{1}H$ NMR (δ vs TMS, 25 °C), 13.8 (C₁), 26.3 (C₄), 27.4 (C₂), 30.1 (C₃), 129.9, 130.00, 132.9, 33.26, 134.00 (Ar-C of PPh₂).

2.4. Synthesis of $[Ru(p-cymene)Cl_2(L)]$ (3)

[RuCl₂(*p*-cymene)]₂ (0.61 g, 1.0 mmol) was taken in 20 cm³ of dichloromethane and a solution of L (0.54 g, 2.0 mmol) in 10 cm³ of dichloromethane was added to it. The mixture was stirred for 2 h at room temperature. The solvent was completely removed on a rotary evaporator under reduced pressure. The residue obtained was dissolved in dichloromethane (5 cm³) and mixed with hexane (30 cm³). The resulting red precipitate (3) was filtered, washed with hexane (3 × 20 cm³) and dried in vacuo. It was recrystallized from dichloromethane–hexane (1:1) mixture. Yield: 80%; m.p.: 89 °C (d). *Anal.* Calc.: C, 53.78, H, 5.68. Found: C, 52.71, H, 5.25%. Molecular weight; found: 620.0, calculated: 580.07; $A_{\rm m}$: 3.80 Ω^{-1} cm² mol⁻¹; ¹H NMR (δ vs TMS, CDCl₃, 25 °C), 1.22–1.33 (m, 9H, H₁ + CH₃ of *i*-Pr), 2.15 (s, 3H, CH₃ of *p*-cymene), 2.29

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(m, 1H, CH of *p*-cymene), 2.81–3.06 (m, 6H, H₄, H₃ and H₂), 7.37–7.72 (m, 10H, Ar-H of –PPh₂); $^{13}C{^1H}$ NMR (δ vs TMS, 25 °C), 12.09 (C₁), 17.11 (CH₃ of *i*-Pr), 20.1 (C₄), 22.3 (CH₃ of *p*-cymene), 28.8 (C₂), 32.5 (CH of *p*-cymene), 33.1 (C₃), 87.9, 91.0 (Ar-C of *p*-cymene), 127.0, 128.3 129.9, 130.3, 132.2, 137.0 (Ar-C of PPh₂).

2.5. X-ray crystallography

The X-ray data for 2 were collected (at 120 K) on an Enraf Nonius Kappa CCD area detector diffractometer, with ϕ and ω scans chosen to give a complete asymmetric unit. Cell refinement [18,19] corresponds to an orthorhombic cell whose dimensions are given in Table 1, along with other experimental parameters. An absorption correction was applied [18,19]. The structure was solved by direct methods [20] and refined using the WinGX version [21] of shelx-97 [22]. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. Non-hydrogen atoms were treated anisotropically. The final cycle of full-matrix least-squares refinement for 2 was based on 4199 observed reflections (3243 for $F^2 > 4\sigma(F^2)$) and 191 variable parameters and converged (largest parameter shift was 0.001 times its esd). The molecular structure of 2 is displayed as an ORTEP diagram in Fig. 1. Its selected bond lengths and bond angles are given in Table 2.

Table 1						
Crystal	data	and	structure	refinement	for 2	

Empirical formula	C ₁₆ H ₁₉ PSBr ₂ Hg
Formula weight	634.75
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	Pbca
a (Å)	13.567(1)
b (Å)	14.859(1)
c (Å)	18.095(1)
$V(\text{\AA}^3)$	3647.6(6)
Z	8
D_{calc} (g/cm ³)	2.312
Absorption coefficient (mm^{-1})	13.014
<i>F</i> (000)	2368
Crystal size (mm ³)	$0.15 \times 0.08 \times 0.02$
θ Range for data collection (°)	3.30-27.53.
Index ranges	$-17 \leq h \leq 17$,
	$-19 \leq k \leq 19$,
	$-23 \leqslant l \leqslant 23$
Reflections collected	29610
Independent reflections (R_{int})	4199 (0.0602)
Maximum and minimum	0.7808 and 0.2456
transmission	
Refinement method	full-matrix least-squares
	on F^2
Data/restraints/parameters	4199/0/191
Goodness-of-fit on F^2	1.036
Final <i>R</i> indices $[F^2 > 4\sigma(F^2)]$	$R_1 = 0.0331, wR_2 = 0.0649$
R indices (all data)	$R_1 = 0.0526, wR_2 = 0.0711$
Largest difference in peak and hole ($e \text{ Å}^{-3}$)	1.001 and -1.162



Fig. 1. Molecular structure of $[HgBr_2(L)]$ (2).

Table 2

Selected	bond	lengths	(A)	and	angles	(°)	for	2

Hg(1)-Br(1)	2.5152(6)	Hg(1)-Br(2)	2.5952(6)
Hg(1) - P(1)	2.415(1)	Hg(1)-S(1)	3.063(1)
S(1)-C(14)	1.811(5)	S(1)-C(15)	1.811(6)
P(1)-C(1)	1.809(5)	P(1)-C(7)	1.810(5)
P(1)-C(13)	1.825(5)		
Br(1)-Hg(1)-P(1)	135.52(4)	Br(2)–Hg(1)–P(1)	119.48(4)
Br(1)-Hg(1)-Br(2)	104.98(2)	P(1)-Hg(1)-S(1)	78.78(4)
Br(1)-Hg(1)-S(1)	92.22(3)	Br(2)-Hg(1)-S(1)	101.23(3)
Hg (1)–P(1)–C(1)	112.6(2)	Hg(1)-P(1)-C(7)	115.3(2)
Hg(1)-P(1)-C(13)	108.5(2)	C(14)-S(1)-C(15)	100.6(3)
C(1)-P(1)-C(7)	107.3(2)	C(1)-P(1)-C(13)	107.4(2)
C(7) - P(1) - C(13)	105.3(2)		
C(7)–C(8)–C(9)	120.0(5)	C(8)-C(9)-C(10)	120.4(5)
C(9)–C(10)–C(11)	120.0(5)	C(10)-C(11)-C(12)	120.6(5)
C(11)-C(12)-C(7)	119.6(5)	C(12)-C(7)-C(8)	119.3(4)

3. Results and discussion

The ligand L, obtained as white crystalline solid, is unstable and is moisture and air sensitive. It can be stored at low temperature ~5 °C in dry nitrogen atmosphere without appreciable decomposition for 2–3 months easily. It is soluble in common organic solvents such as chloroform, dichloromethane and acetone, but is insoluble in hexane. The crystals of 2 are not air and moisture sensitive, but 1 and 3 require storing in a refrigerator to avoid their decay. The complexes are soluble in common organic solvents such as chloroform, dichloromethane and acetone, but are insoluble in hexane. The molar conductance values $\Lambda_{\rm m}$ of the complexes 1–3 in acetonitrile at ~1 mM concentration have been found to be between 3.8 and $6.5 \,\Omega^{-1} \,\mathrm{cm}^2 \,\mathrm{mol}^{-1}$, which are much lower than the values expected for a 1:1 electrolyte. The molecular weights of complexes 2-3, determined in chloroform by the vapour pressure osmometric method, were found to be very close to the values calculated from their molecular formulae. This indicates that there is no appreciable dissociation of these complexes in solution. In the IR spectrum of 1, the band at 248 cm⁻¹ suggests the presence of bridging Cu-Br unit. The IR spectrum of 3 has $v_{sym}(Ru-Cl)$ and v_{asym} (Ru–Cl) at 326 and 294 cm⁻¹, respectively [23,24]. In the ¹H NMR spectrum of L, signals of H₂ and H₃ protons are merged together and appear as a multiplet, whereas the signal of H_4 appears shielded in comparison to those of H_2 and H₃. In the ¹H NMR spectrum of 1, the signals corresponding to H₂ and H₃ get separated and deshielding of the order of 0.2-0.3 ppm is found with respect to the corresponding signals of ligand L. The signal of H_4 appears deshielded by ~ 0.25 ppm in comparison to the corresponding signal of L. Signals for aromatic protons remain unchanged on the formation of 1. In the ¹H NMR spectrum of 2, signals corresponding to all -CH₂ protons merge at 2.66–3.11 ppm, showing deshielding of $\sim 0.35-0.45$ ppm. In the proton NMR spectrum of 3 also, signals of all the CH₂ protons are merged and the average deshielding was found to be ~ 0.5 ppm. The CH₃ signal of the ligand (L) appears to be merged with the CH₃ signal of the isopropyl group of the *p*-cymene ring in the 1 H NMR spectrum of 3. No significant shift occurs in the aromatic protons.

In the carbon-13 NMR spectrum of 1, the C₄ signal is deshielded by ${\sim}0.8~\text{ppm}$ as compared to that of free L. The signals for C_2 and C_1 appear to be deshielded by 1.9 and 1.6 ppm, respectively, with respect to the corresponding signals of free L. In the carbon-13 NMR spectrum of 2, the C_4 signal appears deshielded by 0.68 ppm and the C_3 signal by 1.68 ppm in comparison to those of free L, whereas in the spectrum of 3, the deshielding of the C₂ signal is ~ 1.2 ppm and the other signals do not undergo any significant change in their chemical shifts. The ${}^{31}P \{{}^{1}H\}$ NMR spectra of L, 1, 2 and 3 all have a single peak at -17.0, 31.3, 20.16 and 28.9 ppm, respectively. The signals in the spectra of the complexes are deshielded with respect to that of the ligand. All these NMR data indicate that the interaction of L with Cu(I), Hg(II) and Ru(II) is through both phosphorous and sulfur. With sulfur it may be weak (secondary type), as found out in the case of 2 when its single crystal structure was determined. However, in the case of 1 and 3, which did not give crystals suitable for X-ray diffraction, it could not be ascertained unequivocally.

3.1. Crystal structure

The molecular structure of 2 is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. The ligand L coordinates through phosphorus only, resulting in a coordination number of three for Hg. The three coordination number for mercury is already known

[25–28] and such examples include Hg arsine complexes [25]. The chemistry of Hg-phosphine complexes has been extensively studied by Bell et al. [30], including three coordinate Hg species containing phosphine ligands. However, 2 is the first example of a Hg–(P, S) ligand complex where Hg is three coordinated. The Hg(1)-P(1) bond length of 2.415(1) Å is consistent with the earlier reported values of 2.513(2) and 2.408(2)–2.437(2) Å [29,30]. The Hg(1) \cdots S(1) bond distance [3.063(1)] is shorter than the sum of the van der Waal's radii (3.35 Å). The Hg(1)–Br(1) and Hg(1)– Br(2) bond lengths are 2.5152(6) and 2.5952(6) Å and these are consistent with our earlier observations [31] of 2.505(2)-2.700(2) Å, and 2.528(3) and 2.637(3) Å reported by Bell et al. [30]. The bond angles around Hg are in the range of $78.78(4)-135.52(4)^{\circ}$, with a Br(1)-Hg(1)-Br(2) angle of 104.98(2)° and P(1)-Hg(1)-S(1) angle of 78.78(4)°. However, the sum of the bond angles P(1)-Hg(1)-Br(1), P(1)-Hg(1)-Br(2) and Br(1)-Hg(1)-Br(2) is \approx 360°. Therefore, the Hg, two Br and P atoms are coplanar and the geometry around Hg can be best described as essentially trigonal planar. There is a $Hg \cdots S$ secondary interaction in 2 and the S atom is nearly perpendicular to the plane of the three coordinate Hg-complex. In 2, the C-C bond lengths and bond angles of all the phosphine rings were found to be normal.

4. Conclusion

A relatively simple method is reported for the synthesis of the (P, S) ligand 1-(ethylthio)-2-(diphenylphosphino) ethane (L). Its complexation with Cu(I), Hg(II) and organometallic species of Ru(II) have been explored. The single crystal structure of the Hg(II) complex has been determined. It is found to be a three coordinate species. The sum of the bond angles at Hg, viz. P(1)–Hg(1)–Br(1), P(1)–Hg(1)–Br(2) and Br(1)–Hg(1)–Br(2), is $\approx 360^{\circ}$, and consequently the geometry of Hg can be best described as trigonal planar. There exists a weak secondary interaction between Hg and the S donor site of the ligand [Hg(1)···S(1) bond distance 3.063(1) Å; sum of van der Waal's radii 3.35 Å].

5. Supplementary data

The CCDC No. 602402 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

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