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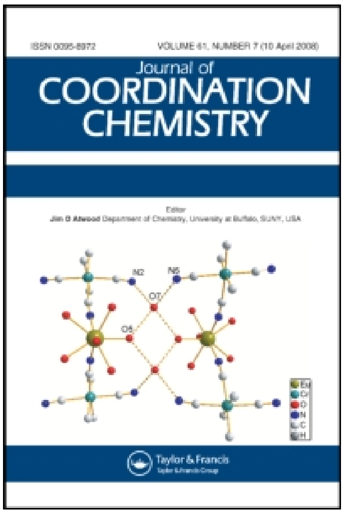

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

METAL-SELENIUM INTERACTIONS. SYNTHESIS AND CRYSTAL STRUCTURE OF [DIIODO{1,1'-METHYLENE-BIS (DIPHENYL PHOSPHINE SELENIDE)}] ZINC(II)

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To cite this Article Lobana, Tarlok S. , Hundal, Rajbir and Turner, Peter(2001) 'METAL-SELENIUM INTERACTIONS. SYNTHESIS AND CRYSTAL STRUCTURE OF [DIIODO{1,1'-METHYLENE-BIS (DIPHENYL PHOSPHINE SELENIDE)}] ZINC(II)', Journal of Coordination Chemistry, 53: 4, 301 — 309

To link to this Article: DOI: 10.1080/00958970108022616

URL: http://dx.doi.org/10.1080/00958970108022616

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J. Coord. Chem., 2001, Vol. 53, pp. 301–309
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METAL-SELENIUM INTERACTIONS. SYNTHESIS AND CRYSTAL STRUCTURE OF [DIIODO{1,1′-METHYLENE-BIS (DIPHENYL PHOSPHINE SELENIDE)}] ZINC(II)

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(Received 12 May 2000)

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Reaction of 1,1′-methylenebis(diphenylphosphine selenide) {$Ph_2P(Se)$—CH_2—$P(Se)Ph_2$, $dpmSe_2$} with zinc(II) diiodide in dry diethylether-benzene mixture formed $ZnI_2(dpmSe_2)$ (1), which has been characterised with the help of analytical data, IR spectroscopy and single crystal X-ray crystallography. Zinc(II) is bonded to two iodine atoms {Zn—I, 2.5732(9), 2.5584(7) Å} and two selenium atoms {Zn—Se, 2.5135(8), 2.4906(10) Å}. The angles about Zn vary from 103.56(3) to 114.69(3) Å, with Se(1)—Zn—Se(2) and I(1)—Zn—I(2) bond angles being 104.57(3) and 114.69(3) Å, respectively. Thus $dpmSe_2$ chelates to Zn(II) forming a distorted tetrahedral geometry about the metal centre. In the six membered metallacyclic ring formed by Zn(1), Se(1), P(1), C(13), P(2) and Se(2) atoms, the angles at Se atoms, namely, Zn(1)—Se(1)—P(1) and Zn(1)—Se(2)—P(2) {96.86(4) and 100.67(5)°, respectively} are the lowest. This reveals higher angular flexibility at Se atom *vis-à-vis* angles at P or C atoms. Complex 1 is the first example of a complex of zinc(II) with a tertiary phosphine selenide ligand, whose structure has been solved.

Keywords: Phosphine selenide; Zinc(II) iodide; Crystal structures

INTRODUCTION

The coordination chemistry of tertiary phosphine chalcogenides has been the focus of several investigations and this interest stems from bonding and

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*Corresponding author.

structure, catalytic and extractive metallurgy aspects. The molecular structures of several phosphine oxide and sulphide complexes have been solved [1, 2]. The structural chemistry of phosphine selenides has not received the attention it deserves, the major reason being the poor solubility of the complexes reported [1, 2].

We have been interested in the spectroscopic and structural chemistry of metal-sulphur interactions involving phosphine sulphides, heterocyclic thiones and thiosemicarbazones [3]. As an extension of our interest in the structural chemistry of metal-selenium interactions and the importance of this study in metal-organic chemical vapour deposition (MOCVD) [4], work on phosphine selenide reactions with metal salts has been initiated. It may be pointed out that there are only two reports on structural characterisation of metal-phosphine selenide compounds [5, 6]. Here we report the synthesis and characterisation of zinc(II) diiodide complex with 1,1′-methylenebis(diphenylphosphine selenide) $\{Ph_2P(Se)—CH_2—P(Se)Ph_2, dpmSe_2\}$ and this represents the first example of a structurally characterised zinc(II) complex with a tertiary phosphine selenide (I and II).

R_3PSe $R_2P(Se)—(CH_2)_m—P(Se)R_2$

I II

$\{R = Ph, etc., m = 1, 2, etc.\}$

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EXPERIMENTAL

Materials and Techniques

Zinc(II) iodide was prepared *via* a reported method by reacting zinc dust with iodine in dry diethylether [7]. Bis(diphenylphosphino)methane ($Ph_2PCH_2PPh_2$, dpm) was procured from Aldrich. The diselenide (*viz*, $dpmSe_2$) was made by refluxing dpm with Se metal (1 : 2 mol ratio) in benzene or toluene. C and H determination was performed with a Carlo-Erba 1108 microanalyser at the University of Santiago, Spain. Infrared spectra have been recorded as KBr pellets in the range 4000–200 cm^{-1} on a Philips Analytical SP3-300 spectrophotometer.

$[ZnI_2(dpmSe_2)] \cdot 0.5C_6H_6$

To a solution of zinc(II) iodide (0.090 g, 0.16 mmol) in a 10 ml mixture of dry diethylether-benzene (2 : 1 v/v ratio) was added a solution of $dpmSe_2$

(0.053 g, 0.16 mmol) in 10 ml of dry benzene. The mixture was refluxed for about 2 hours and the colourless precipitates formed were filtered, washed with diethylether-benzene mixture and finally dried *in vacuo*. Yield 70%, m.p. 264-66°C. *Anal.* Found: C, 37.53; H, 3.00. Calc. for $C_{28}H_{25}P_2Se_2I_2Zn$: C, 37.33; H 2.80%. Crystals were grown from a benzene-ethanol mixture.

Crystal Structure Determination

A colourless bladed crystal was attached to a thin fibre and mounted on a Bruker SMART 1000 CCD diffractometer employing graphite-monochromated MoK_α radiation. Cell constants were obtained from least-squares refinement against 7821 reflections with 2θ between 4.40 and 52.38°. Data were collected at 297(2) K with 0.3° incremental ω scans to 56.54° 2θ. The intensities of 325 standard reflections recollected at the end of the experiment did not change significantly during the data collection. An empirical absorption correction determined with SADABS [8] was applied to the data. Data integration and reduction was undertaken with SAINT and XPREP [9], and subsequent computations were carried out with the

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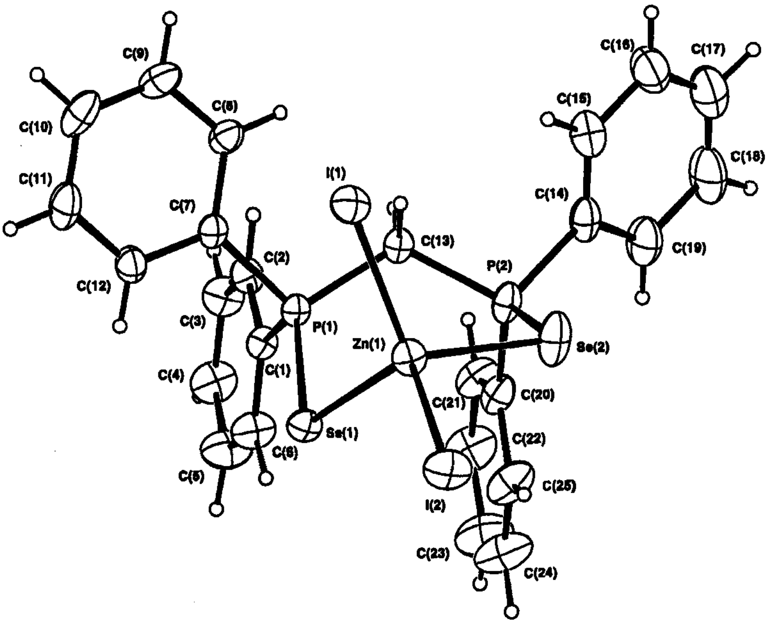

FIGURE 1 Structure of $[ZnI_2(dpmSe_2)] \cdot 0.5C_6H_6$ (1) showing the numbering scheme.

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TABLE I Crystal data and refinement details for $[ZnI_2(dpmSe_2)]0.5C_6H_6$ (1)

Empricial formula	$C_{28}H_{25}I_2P_2Se_2Zn$		
Molecular weight	900.51	Crystal size/mm	0.296 × 0.130 × 0.036
Wavelength Å	0.71073	$2\theta_{max}/°$	56.54
Crystal system	monoclinic	Index ranges	$-16 < = h < = 16, -18 < = k < = 18,$ $-25 < = l < = 25$
Space group	$P2_1/n$		
Unit cell dimensions		Reflections collected	29656
a/Å	12.2049(5)	Independent reflections	7597
b/Å	13.6461(6)	R_{int}	0.0461
c/Å	19.4426(8)	Reflections observed $[I > 2\sigma(I)]$	4751
β/°	102.2070(10)		
Volume/Å	3164.9(2)		
Z	4	Goodness of fit on F^2	1.031
Density (calculated) (Mgm^{-3})	1.890	Final R indices $[I > 2\sigma(I)]$*	$R1 = 0.045$, $wR2 = 0.116$
Absorption coefficient/cm^{-1}	5.144		

* $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_c^2)'/\Sigma(wF_c^2)^2)^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 4.9999P]$ where $P = (F_o^2 + 2F_c^2)/3$.

teXsan [10] graphical user interface. Data reduction included the application of Lorentz and polarisation corrections.

The structure was solved in the space group $P2_1/n$ by direct methods with SIR97 [11], extended and refined with SHELXL-97 [12]. The asymmetric unit contains a complex molecule together with half of a benzene molecule centred about an inversion site. Anisotropic displacement parameters were refined for the non-hydrogen atoms and a riding atom model was used for the hydrogen atoms included in the model. The population of the benzene solvate atoms refined to 1.001 and was accordingly fixed at 1.0. An ORTEP [13, 14] depiction of the molecule is provided in Figure 1. Crystal data are collected in Table I, and final coordinates for non-hydrogen atoms in Table II.

TABLE II Final coordinates, for the non-hydrogen atoms

Atom	x/a	y/b	z/c	U_{eq}(Å^2)
I(1)	0.2276(3)	0.63269(3)	0.16432(2)	0.07400(14)
I(2)	−0.01363(4)	0.82029(3)	0.23786(3)	0.09022(18)
Se(1)	−0.08235(5)	0.52268(4)	0.19646(3)	0.05769(16)
Se(2)	0.14277(8)	0.61080(4)	0.36253(4)	0.0941(3)
Zn(1)	0.06867(6)	0.64814(4)	0.23584(4)	0.06000(18)
P(1)	0.02629(11)	0.39712(9)	0.20438(7)	0.0460(3)
P(2)	0.13477(15)	0.45395(10)	0.36105(7)	0.0609(4)
C(1)	−0.0498(4)	0.2862(3)	0.2137(3)	0.0495(12)
C(2)	0.0071(5)	0.1978(4)	0.2142(3)	0.0604(14)
C(3)	−0.0455(6)	0.1107(4)	0.2229(4)	0.0763(18)
C(4)	−0.1525(6)	0.1099(5)	0.2304(4)	0.088(2)
C(5)	−0.2096(6)	0.1959(5)	0.2279(4)	0.096(2)
C(6)	−0.1580(5)	0.2858(4)	0.2218(4)	0.0761(18)
C(7)	0.0828(4)	0.3794(3)	0.1269(3)	0.0492(12)
C(8)	0.1932(5)	0.3525(4)	0.1295(3)	0.0649(15)
C(9)	0.2304(6)	0.3419(5)	0.0677(4)	0.082(2)
C(10)	0.1608(8)	0.3565(5)	0.0043(4)	0.090(2)
C(11)	0.0511(7)	0.3800(5)	0.0008(3)	0.086(2)
C(12)	0.0117(5)	0.3920(4)	0.0615(3)	0.0672(15)
C(13)	0.1481(4)	0.4024(3)	0.2764(2)	0.0515(12)
C(14)	0.2569(6)	0.4093(4)	0.4232(3)	0.0714(17)
C(15)	0.3606(7)	0.4195(6)	0.4081(4)	0.092(2)
C(16)	0.4563(8)	0.3901(7)	0.4557(5)	0.109(3)
C(17)	0.4463(10)	0.3531(7)	0.5178(5)	0.114(3)
C(18)	0.3456(10)	0.3409(7)	0.5345(4)	0.121(3)
C(19)	0.2468(7)	0.3685(5)	0.4866(4)	0.096(2)
C(20)	0.0113(6)	0.4046(4)	0.3840(3)	0.0710(17)
C(21)	0.0018(6)	0.3037(5)	0.3925(3)	0.0805(19)
C(22)	−0.0935(8)	0.2646(6)	0.4104(4)	0.108(3)
C(23)	−0.1776(9)	0.3277(7)	0.4188(5)	0.126(3)
C(24)	−0.1698(9)	0.4263(7)	0.4098(5)	0.127(3)
C(25)	−0.0758(8)	0.4654(6)	0.3924(4)	0.098(2)
C(26)	0.4022(16)	0.5439(15)	0.0051(19)	0.187(7)
C(27)	0.468(3)	0.5038(19)	0.0606(12)	0.183(8)
C(28)	0.563(3)	0.4562(15)	0.0578(12)	0.186(6)

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RESULTS AND DISCUSSION

General Comments

Zinc(II) chloride and bromide are hygroscopic and their coordination chemistry is tedious; thus efforts to obtain suitable crystals of their reaction products with tertiary phosphine selenides did not succeed. The choice of iodide as anion was expected to serve two purposes, to enhance the soft character of zinc(II) and to reduce the hygroscope nature of zinc(II). Thus from zinc(II) diiodide and 1,1′-methylenebis(diphenylphosphine selenide) {$Ph_2P(Se)—CH_2—P(Se)Ph_2$, dpmSe$_2$} suitable crystals of the complex were obtained from ethanol-benzene mixture. Significanly, acetonitrile displaced the dpmSe$_2$ ligand from the coordination sphere. The poor solubility of the complex in chloroform prevented NMR studies in solution.

IR spectra of the ligand and the complex were very similar with little or no change in peak positions pertaining to various groups. The diagnostic $\nu P=Se$ peak appears at $520\,cm^{-1}$ in the ligand and at $525\,cm^{-1}$ in the complex and from this it is difficult to know whether there is any interaction between Zn and Se. To establish this interaction, a single crystal X-ray study has been undertaken.

Crystal and Molecular Structure

The atom numbering scheme of [ZnI$_2$(dpmSe$_2$)]0.5C$_6$H$_6$ (**1**) is shown in Figure 1. Table III lists important bond lengths and angles. The basic unit is [ZnI$_2$(dpmSe$_2$)] with no evidence for intermolecular interactions. However, the benzene molecule is positioned centrosymmetrically between two complex molecules Figure 2.

TABLE III Selected bond lengths (Å) and angles (°) for **1**

Zn(1)—I(1)	2.5732(9)	P(1)—C(1)	1.805(5)
Zn(1)—I(2)	2.5584(7)	P(1)—C(7)	1.802(5)
Zn(1)—Se(1)	2.5135(8)	P(2)—C(14)	1.814(7)
Zn(1)—Se(2)	2.4906(10)	P(2)—C(20)	1.791(7)
P(1)—Se(1)	2.1520(13)	P(1)—C(13)	1.816(5)
P(1)—Se(2)	2.1426(15)	P(2)—C(13)	1.828(5)
Zn(1)—Se(1)—P(1)	96.86(4)	Se(1)—Zn(1)—Se(2)	104.57(3)
Zn(1)—Se(2)—P(2)	100.67(5)	Se(2)—Zn(1)—I(1)	111.32(4)
Se(1)—Zn(1)—I(2)	111.41(3)	Se(1)—Zn(1)—I(1)	110.62(3)
Se(2)—Zn(1)—I(2)	103.56(3)	I(2)—Zn(1)—I(1)	114.69(3)
Se(1)—P(1)—C(13)	114.54(16)	Se(2)—P(2)—C(13)	112.59(17)
P(1)—C(13)—P(2)	119.7(3)		

Symmetry operators: (1)x,y,z; (2)$-x+1/2$, $y+1/2$, $-z+1/2$; (3)$-x,-y,-z$; (4)$x-1/2$, $-y-1/2$, $z-1/2$.

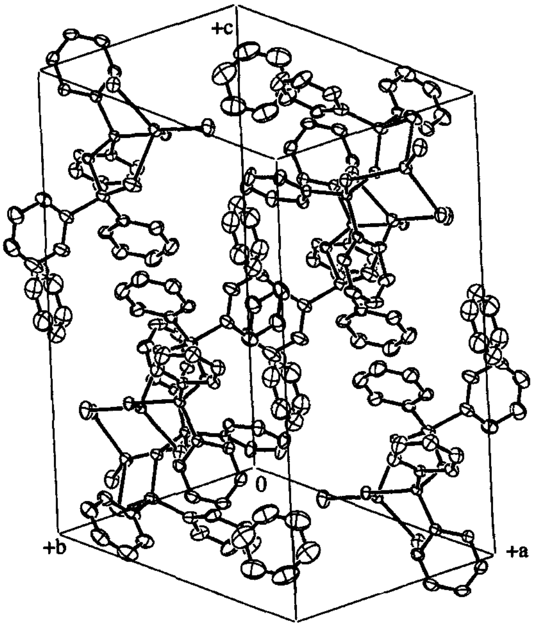

FIGURE 2 Molecular packing arrangement of [ZnI$_2$(dpmSe$_2$)] • 0.5C$_6$H$_6$ (1).

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Two Se atoms of the chelating dpmSe$_2$ ligand and two iodine atoms coordinate to Zn and the geometry about Zn centre can be described formally as being on distorted tetrahedral. The angles about Zn vary from 103.56(3) to 114.69(3)° with Se(2)—Zn(1)—I(2) being the smallest and I(1)—Zn(1)—I(2) the largest. In the six membered metallacyclic ring formed from Zn(1), Se(1), P(1), C(13), P(2) and Se(2) atoms, the angles at Se, namely, Zn(1)—Se(1)—P(1) and Zn(1)—Se(2)—P(2) {96.86(4) and 100.67(5)° respectively} are the smallest. This reveals higher angular flexibility at Se atom *vis-à-vis* the angles at P or C atoms.

Zn—Se bond distances {2.5138(8), 2.4906(10) Å} differ marginally and are longer than required by the sum of covalent radii for a single Zn—Se bond {2.37 Å} but much shorter than the sum of van der Waals radii {3.30Å} [15]. The average P=Se bond distance is 2.1473(14) Å, shorter than the sum of covalent radii of P and Se atoms {2.27Å}. This distance is longer than the P=Se distances of 2.106(1)–2.109(5) Å observed in the free ligands [16, 17]. This shows that the P—Se bond is weakened in its complexes with metals; lack of shifts in the IR spectrum for the diagnostic νP=Se peak could be due to the relatively low sensitivity of the heavier Se atom to coordination changes. Other significant bond distances of the metallacyclic ring, namely

P(1)—C(13) and P(2)—C(13) are longer than P—C_{Ph} bond distances and this is attributed to the π electron density on phenyl rings. Finally Zn—I bond distances {2.5732(9), 2.5584(7) Å} are close to the sum of covalent radii {2.53Å}.

Acknowledgements

Financial assistance from the CSIR and provision of laboratory facilities (to RH) by the Guru Nanak Dev University (Amritsar 143 005) are gratefully acknowledged.

Supplementary Data

Full lists of crystallographic data may be obtained from the authors upon request.

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