

INFLUENCE OF LONE-PAIR ACTIVITY ON THE BOND PARAMETERS OF
LEAD BROMIDE, LEAD CHLORIDE AND LEAD OXIDE

BADAR SALIM HAMED AL MAAMARI

UNIVERSITI TEKNOLOGI MALAYSIA

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BADAR SALIM HAMED AL MAAMARI

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I dedicate this project to my dear parents. Also, my family specially my dear wife and my children

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ABSTRACT

Lead Pb(II) is challenging environment to study because it has electron lone pair, coordination number would vary from 2 to 10. The current study chooses chlorine, oxygen and bromine as coordination atoms because it bonded with one type of element in single crystal. The present research work is focused, to study the impact of electron lone pair on coordination number (CN), bond length and bond valence sum(BVS). The coordination number is the number of atom attachment with cation, which represents the central atom. The sample of the study includes 388 sites of Pb(II). Analysis of those sites consist of three types of single crystals; 44 of single-crystal Pb-O, 24 of single crystal Pb(II)-Cl and 18 of single crystal Pb(II)-Br (Uses for that different programs like Origin, Excel, Avogadro and Crystal Maker). Deduced through the graph (coordination number-frequency) lead prefers to bond with two or eight atoms of oxygen. Also, it is noted that lead prefers to bond with two atoms of chlorine while prefer to bond with five or six atoms of bromine. The pattern that lead follows in (coordination number-frequency), (bond length-frequency) and (bond valence sum-frequency) indicate that high value of bond length offset low bond valence sum and high coordination number while the low value of bond length offset high bond valence sum and low coordination number. This interpretation is according to distortion theory. Study correlations (LP magnitude – coordination number), (LP magnitude – bond length R) and (LP magnitude – bond valence sum) lead to confirm that the presence electron lone pair spread the values of coordination number, bond length and bond valence sum. The graph of coordination number energy is confirm on the fact that the crystal prefers a specific coordination number to be stable(less energy). Lone pair divided in two types active lone pair and non-active lone pair. When LP magnitude = 0, lone pair will not be active and there are symmetric bonds while when LP magnitude > 0, LP will be active and non – symmetric bonds.

ABSTRAK

Plumbum Pb(II) adalah sukar untuk dikaji di alam sekitar kerana mempunyai elektron pasangan tersendiri, nombor koordinatan berubah antara 2 ke10. Kajian ini tertumpu dalam mengkaji impak elektron pasangan tersendiri terhadap nombor koordinatan (CN), panjang ikatan, dan ikatan valens (BVS). Sampel kajian terdiri daripada 388 tapak Pb(II). Analisa terhadap tapak tersebut mendapati 3 jenis hablur tunggal, yang terdiri daripada 44 hablur tunggal Pb-O, 24 hablur tunggal Pb(II)-Cl dan 18 hablur tunggal Pb(II)-Br. Kajian ini telah menggunakan perisian seperti, *Origin, Excel, Avogadro and Crystal Maker*. Deduksi daripada graf (frekuensi nombor koordinatan), Plumbum gemar mengikat dengan dua atau lapan atom oksigen. Begitu juga, Plumbum juga gemar mengikat dengan 2 atom klorin disamping mengikat dengan 5 atau 6 atom Bromin. Corak yang diikuti Plumbum berdasarkan graf frekuensi nombor koordinatan, frekuensi panjang ikatan, dan jumlah ikatan valens, menunjukkan nilai yang tinggi bagi pajang ikatan menyebabkan ofset terhadap jumlah ikatan valens yang rendah dan nombor koordinatan yang tinggi. Di samping itu, nilai pajang ikatan yang rendah menyebabkan ofset pada jumlah ikatan valens yang tinggi dan nombor koordinatan yang rendah. Tafsiran ini adalah berdasarkan *Distortion Theory* (Teori penyelewangan). Seterusnya, kajian terhadap korelasi magnitud LP - nombor koordinatan (*LP magnitude – coordination number*), magnitud LP – panjang ikatan R (*LP magnitude – bond length R*) dan magnitud LP – jumlah ikatan valens (*LP magnitude – bond valence sum*) mengesahkan kehadiran elektron pasangan tersendiri menyebabkan rebakan pada nilai-nilai nombor koordinatan, panjang ikatan, dan jumlah ikatan valens. Plot graf bagi nombor koordinatan dan tenaga mengesahkan bahawa hablur mengutamakan nombor koordinatan yang spesifik bagi pengstabilan (tenaga rendah). Pasangan bersendiri dibahagikan kepada dua jenis yang terdiri daripada pasangan bersendiri-aktif dan pasangan bersendiri-tidak aktif. Akhir sekali, apabila magnitud LP = 0, pasangan bersendiri menjadi tidak aktif dan ikatan yang simetri terjalin. Selain itu, sekiranya magnitud LP > 0, pasangan bersendiri menjadi aktif dan ikatan tidak simetri terjalin.

TABLE OF CONTENTS

TITLE	PAGE
DECLARATION	iii
DEDICATION	iv
ACKNOWLEDGEMENT	v
ABSTRACT	vi
ABSTRAK	vii
TABLE OF CONTENTS	xi
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	xvii
CHAPTER 1 INTRODUCTION	
1.1 Introduction	1
1.2 Problem Statement	3
1.3 Objective of Study	4
1.4 Scope of the Research	4
1.5 Research Significance	5
CHAPTER 2 LITERATURE REVIEW	
2.1 Bond Valence Method	7
2.2 VSPER model	8
2.3 Lone pair (LP)	9
2.4 Holodirected or Hemidericted in crystal	11
2.5 Hybridization and Lone pair (LP)	12
2.6 Distortion Theorem	14
2.7 Bond length and coordination number	15

2.8	Energy	26
2.9	Frictional coordinates and orthogonal coordinates	28

CHAPTER 3 RESEARCH METHODOLOGY

3.1	Introduction	29
3.2	Data	29
3.3	Classification of data	30
3.4	Crystal definition	30
3.5	Calculating Bond Valence Sum	35
3.6	Calculating Lone Pair magnitude	36
3.7	Frequency of Coordination Number (CN)	39
3.7	Frequency of Bond Valence Sum (BVS)	42
3.8	LP magnitude charts	45
3.9	Energy and Coordination number	46

CHAPTER 4 RESULTS

4.1	Pb(II)-O pair	51
4.1.1	Pb(II)-O pair parameters (R_o , b)	51
4.1.2	Pb(II)-O coordination number	50
4.1.3	Pb(II) bond valence sum	52
4.1.4	Pb(II)-O bond distance R_{Pb-O}	54
4.1.5	Pb(II) lone pair activity	56
4.1.4.1	n_{PbO} (LP)	56
4.1.4.2	R_{Pb-O} (LP)	58
4.1.4.3	Bond Valence Sum(LP)	59
4.1.5	[PbO _n] Minimum Energy	60
4.1.6	Lone pairs vectors Pb(II)-O	61
4.1.6.1	LP vectors > 0	61
4.1.6.2	LP vectors = 0	64
4.2	Pb(II)-Cl pairs	65

4.2.1	Pb(II)-Cl pair parameters (R_o , b)	65
4.2.1	Pb(II)-Cl coordination number $n_{\text{Pb-Cl}}$	65
4.2.2	Pb(II)-Cl bond valence sum	67
4.2.3	Pb(II)-Cl bond length $R_{\text{Pb-Cl}}$	68
4.2.4	Pb(II) lone pair activity	69
4.2.4.1	$n_{\text{Pb-Cl}}(\text{LP})$	70
4.2.4.2	$R_{\text{Pb-Cl}}(\text{LP})$	70
4.2.4.3	Bond valence sum(LP)	71
4.2.5	$[\text{PbCl}_n]$ minimum energy	72
4.2.6	Lone pair vector Pb(II)-Cl	72
4.2.6.1	LPvector > 0	74
4.2.6.2	LP vector = 0	74
4.3	Pb(II)-Br pairs	75
4.3.1	Pb(II)-Br pairs parameters (R_o , b)	75
4.3.2	Pb(II)-Br coordination number	75
4.3.3	Pb(II) bond valence sum	76
4.3.4	Pb(II)-Br bond length $R_{\text{Pb-Br}}$	77
4.3.5	Pb(II) lone pair activity	78
4.3.4.1	$n_{\text{Pb-Br}}(\text{LP})$	78
4.3.4.2	$R_{\text{Pb-Br}}(\text{LP})$	79
4.3.4.3	Bond valence sum(LP)	79
4.3.5	$[\text{PbBr}_n]$ minimum energy	80
4.3.6	Lone pair vector Pb(II)-Cl	81
4.2.6.1	LP vector >0	81
4.2.6.2	LP vector = 0	82

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1	Conclusions	83
5.2	Future Recommendation	84
	REFERENCES	85

LIST OF TABLES

TABLE NO	TITLE	PAGE
Table 2.1	The shape of molecules change by the effect of lone pair	10
Table 2.2	Stats about Lead Pb(II) and Pb(IV)	19
Table 3.1	Bond distance (R) for Pb(II)-Br	35
Table 3.2	Pb(II)-Br parameters	35
Table 3.3	Calculate bond valence and bond valence sum	36
Table 3.4	Values of both type of coordinates for the single crystal (Pb1 1010210)	37
Table 3.5	The result calculate vector in single-crystal (Pb1 1010210)	37
Table 3.6	Result of distance in single-crystal (Pb1 1010210)	38
Table 3.7	Values of X , Y , and Z for net vector in the single crystal (Pb1 1010210)	38
Table 3.8	Some value of coordination number	39
Table 3.9	The result of CN frequency	39
Table 3.10	Some value of BVS	42
Table 3.11	Results of calculating energy	49
Table 4.1	Coordination number (n_{PbO}) and energy	60
Table 4.2	Coordination number (n_{PbCl}) and energy	74
Table 4.3	Coordination number (n_{PbBr}) and energy	80

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
Figure 2.1	Central atom bonded with four atoms opposite side located electron lone pair	8
Figure 2.2	HF molecular	9
Figure 2.3	(a) Lone Pair is non active and (b) lone pairs is active	9
Figure 2.4	Holodirected and Hemidericted	11
Figure 2.5	Symmetrical bonds of Pb^{2+} in Pb	12
Figure 2.6	Energy level diagram of Pb-O showing the hybridization between Pb 6 <i>S</i> and O 2 <i>P</i> states	13
Figure 2.7	Non-symmetrical bonds of Pb^{2+} in Pb-O	13
Figure 2.8	Interaction between (a) Pb 6 <i>s</i> and O 2 <i>p</i> orbitals and (b) the Sn and O 2 <i>p</i>	14
Figure 2.9	Bond valence, bond length curve	15
Figure 2.10	Bond length distortion as a function of coordination number	17
Figure 2.11	Correlation between coordination number and mean bond length	17
Figure 2.12	Values of bond valence sum for different valence sum	18
Figure 2.13	Pb(II) bonded charts with O^{2-} (X-axis)bond length (Y-axis) frequency	20
Figure 2.14	The correlation between bond length distortion and coordination number for (a) Se^{4+} and Pb^{2+} as Figure 2.8 appear is inverse correlation	22
Figure 2.15	Bond length distortion as a function of coordination number	22
Figure 2.16	Bond length distortion as a function of coordination number	23
Figure 2.17	The effect of sample size on (a) mean bond length, (b) standard deviation of the mean bond length, (c) skewness and (d) kurtosis	24
Figure 2.18	The correlation between mean bond valence and mean bond length	25

Figure 2.19	Correlation of Bond-valence sum and coordination number for (a) the alkali metal and (b) alkaline-earth-metal ions by using parameter of Gagne' & Hawthorne (2015)	26
Figure 3.1	The shaded pane represents the downloaded file	29
Figure 3.2	A collection of files	30
Figure 3.3	Opening the file (1010210.cif)	31
Figure 3.4	Crystal structure (1010210.cif)	31
Figure 3.5	Single crystal Pb(II)-Br include two lead atoms	31
Figure 3.6	Single crystal Pb(II)-Br	32
Figure 3.7	List coordinates option	33
Figure 3.8	List coordinates	33
Figure 3.9	Previous coordinate list in Exel	33
Figure 3.10	Distance button	34
Figure 3.11	Distance page	34
Figure 3.12	Distance value in Excel page	40
Figure 3.13	The value of table 3.8 in the Origin program	40
Figure 3.14	Column icon	40
Figure 3.15	Graph (CN-frequency)	41
Figure 3.16	Fitting option	41
Figure 3.17	Pattern of spread values of CN	42
Figure 3.18	Data analysis option	42
Figure 3.19	Option menu in data analysis	43
Figure 3.20	List of data for obtaining Histogram	44
Figure 3.21	Histogram BVS for Pb(II)-Br	45
Figure 3.22	Graph of BVS	45
Figure 3.23	Organized data in Excel page	45
Figure 3.24	Data of Pb(II)-Br	46
Figure 3.25	Scatter Option	46
Figure 3.26	Correlation (LP magnitude- Bond valence sum)	47
Figure 3.27	Uesre interface Avogadro program	47

Figure 3.28	Eelement option	47
Figure 3.29	Oxygen molecular with two coordination number	48
Figure 3.30	Measure energy	48
Figure 3.31	Data of Pb(II)-Br	49
Figure 3.32	Relationship between coordination number and energy	50
Figure 4.1	Charts (Coordination number- Frequency) for (Pb(II)-O) by use three-parameter	52
Figure 4.2	Charts (Bond valence sum - Frequency) for (Pb (II)-O) by using three-parameter	53
Figure 4.3	Bond-valence-bond-length correlation	55
Figure 4.4	Chart (<i>R</i> -Frequency) for (Pb(II)-O) by using three parameter	56
Figure 4.5	(A) Holodirected and (B) Hemidirected coordination	57
Figure 4.6	Correlation (LP magnitude - coordination number) for (Pb (II)-O)	58
Figure 4.7	Correlation (LP magnitude - <i>R</i>) for (Pb (II)-O)	59
Figure 4.8	Correlation (LP magnitude - coordination number) for (Pb (II)-O)	60
Figure 4.9	Graph (Energy – coordination number)	61
Figure 4.10	Charts appear lone pairs vector in single crystal Pb(II) -O	66
Figure 4.11	Charts appear LP magnitude equal zero in single crystal Pb(II) -O	66
Figure 4.12	Charts (Coordination number- Frequency) for (Pb(II)-Cl) by using three-parameter	67
Figure 4.13	Charts (Coordination number- Frequency) for (Pb(II)-Cl) by using three-parameter.	68
Figure 4.14	Charts (<i>R</i> -Frequency)for Pb(II)-Cl by using two parameter.	70
Figure 4.15	Correlation (LP magnitude - coordination number) for (Pb (II)-Cl)	71
Figure 4.16	Correlation(LPmagnitude- <i>R</i>)for(Pb(II)-Cl)	72
Figure 4.17	Correlation (LP magnitude - coordination number) for (Pb (II)-Cl)	73
Figure 4.18	Chart appear relationship between Energy and coordination number	74

Figure 4.19	Charts appear lone pairs vector in single crystal Pb(II)–Cl	76
Figure 4.20	Charts appear LP magnitude equal zero in single crystal Pb(II)–Cl	77
Figure 4.21	Charts (Coordination number–Frequency) for Pb(II)–Br by apply two-parameter	78
Figure 4.22	Correlation between Bond valence and Frequency for Pb(II)–Br by apply two parameter	79
Figure 4.23	Charts (<i>R</i> - Frequency) for (Pb(II)-Br) by using two-parameter	80
Figure 4.24	Correlation (LP magnitude - coordination number) for (Pb (II)-Cl)	81
Figure 4.25	Correlation (LP magnitude – Bond bond distance) for (Pb-Cl)	82
Figure 4.26	Correlation (LPmagnitude-Bond valence sum) for (Pb(II)-Br)	82
Figure4.27	Chart appear relationship between Energy (Mean) and coordination number	82
Figure 4.28	Influence of LP in Pb(II)-Br	85
Figure 4.29	LP equal to zero in Pb(II)-Br	86

LIST OF ABBREVIATIONS

Å	-	Angstrom
BVS	-	Bond valence sum
CN	-	Coordination number
ELP		Electron Lone pair
LP	-	Lone pair
R_o	-	Bond length
S_{ij}	-	Bond valence for R_{ij}
v.u	-	Valence unit
V	-	valency of central atom in single crystal

CHAPTER 1

INTRODUCTION

1.1 Introduction

In the second half of 19th-century scientists developed, a new concept in chemistry called the valency. The valency of an atom is defined as a degree of electron sharing when an atom is bonded with other atoms or group of atoms to form chemical bonds.

The development of valency leads us to new theories of chemical bonding including Lewis structure (1916), valence bond theory (1927) and valence shell electron pair repulsion (VSEPR) theory (1958). All these theories have helped the scientists to determine the factors that affect the molecular shapes.

Therefore, understanding these factors are important for predicting stable structures. Nowadays, all of these attempts unite lab experiments and computer simulation to obtain a stable crystal structure (Adams, 2014).

What controls structure stability? Pauling in 1929 advises us to study the behavior of bond length to find the answer. In 1979, Glasser tried to find the answer why some compounds exist while others cannot? Questions like those push us deeper into the structural world (Gagne, 2015). In 1957, Gillespie and Nyholm explained the influence of lone pair in the dimensional shape of molecular which is known as valence shell electron pair repulsion (VSEPR) theory.

In 1988, Brown used the Pauling radius ratio to find coordination numbers, which represents the number of anions that bonded with the central atom. Coordination number is equal to the cation radius divided by anion radius. He explained that energy reaches to the lowest possible energy at a specific distance between the two bonded atoms (Brown, 1988). The following year, endeavor Victor

and Wolfgang studied the effect of electron lone-pair on nuclear spin-spin coupling constants (Gil and Philipsborn, 1989).

Research did not stop there but sought other relevant studies. In 1998 Liat Shimoni and others studied the influence of lone electron pair in Pb^{2+} and as a result, the relationship between lead crystal geometry and the coordination number was found (Shimoni-Livny *et al.*, 1998).

In 2005, Aron Walsh and Greame studied the effect of active lone pair on PbO and PbS . The researchers reached a conclusion that lone electron pair was not the reason for distortion of Pb(II) crystal but because of electron density (Walsh and Watson, 2005). Joseph and others studied compound $\text{Na}_3[\text{Pb}(1,4,7,10\text{-tetraazacyclododecane-1,4,7,10-tetraacetate})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ the shape of single crystal Pb(II)-O under influence of a stereochemically active lone pair (Nugent *et al.*, 2015). Given this disparity on the effect of the electron lone pair, the current study attempt to remove uncertainty on this dimension.

The current study is a continuation of research conducted on lead Pb(II) . The main goal is to study the influence of lone electron pair on Pb(II) when lead forms a bond with Br, Cl, and O. Current thesis achieves object by analysis of the Inorganic Crystal Structure Database (ICSD) which, related to Pb(II)-Cl , Pb(II)-Br and Pb-O , this will be applied to analyze data using programs like Origen, Avogadro, and EXCEL.

1.2 Problem Statement

A previous study focused on the impact of electron lone pair on the geometry of a single crystal which includes Pb(II) . Gagne and Hawthorne studied groups of ion bonded to oxygen, which has active lone pair (Gagne and Hawthorne, 2016). The study mentioned that there is a weak correlation between bond length and coordination number. Furthermore, Gagne and Hawthorne provided a statistical

study when they deal with coordination number, bond valence and bond length (Gagne and Hawthorne, 2016)

Another study for the same researcher studied 84 configurations of the lanthanide ions bonded to oxygen (Gagne, 2018). In addition to these, there is no illustration of the electron lone pair role towards the distortion of bond-length and bond valence (Gagne, 2018). In addition to this, another study showed variation of the value of bond-length especially for ion that has stereoactive lone pair electron but they did not introduce convincing explanation about that (Gagne and Hawthorne, 2018). Furthermore, Gagne and Hawthorne study confirms there is no relationship between lone pair stereoactivity and coordination number (Gagne and Hawthorne, 2018).

Gagne and others(2018) also mentioned that there is no strong correlation between lone pair and coordination number (Gagne *et al.*, 2018). In addition, the same situation happened between bond valence sums at the central cation and electron lone pair (Gagne and Hawthorne, 2018). Walsh and others deduced the distorted Pb(II) crystal geometry not for lone pair but for the reason of electron distribution surround lead atoms (Walsh *et al.*, 2011).

On the other hand, Orgel (1959) explained lone pair distortion through the mixing of non-bonding *s* and *p* orbitals. In this model, the distorted coordination around lone pair cations was explained by the hybridization (Orgel, 1959). Baranyi(1977) found that there is an influence of lone pair on spread of values of coordination number(Baranyi *et al.*, 1977). A linear correlation between mean bond length and coordination number was observed in the presence of lone pair (Fabini *et al.*, 2016). Valadbeigi(2018) was studied the interaction of H₂O, H₂S, H₂Se, NH₃, PH₃, and AsH₃ with cations H⁺, CH³⁺, Cu⁺, Al³⁺, Li⁺, Na⁺, and K⁺ from the energetic and structural viewpoint. He was deduced that the lone pair change(H-M-H) angles(M=N, P, As, O, S and Se) (Valadbeigi *et al.*, 2018).

Studies agree that electron lone pair play an important role in crystal geometry. On the other hand, others did not explain the mechanism by which this effect occurs. In general, most of the research focuses on increasing the quantity of

data by use of statistics when dealing with these topics. Often the interpretation is done on a statistical basis, without reference to previous theories such as distortion theory or VSPER theory. Most previous studies did not study the effect of electron lone pair (ELP) on coordination number, bond valence sum and bond length in different parameters. The current study will show the effect of lone pair by using bond valence method to determine coordination number (CN) and bond valence sum in different bond valence parameters.

1.3 Objective of the Study

This study focuses on bonds of Pb(II)-O, Pb(II)-Cl and Pb(II)-Br to reach the following primary objectives:

- i. Finding the distribution of the frequency of bond valence sum(BVS), coordination number(CN), and bond length(R_{ij})
- ii. Studying the relationship between lone pair(LP) magnitude and (CN, BVS, bond length)

1.4 Scope of the Research

The scope of the study is limited on Pb^{2+} bonded with O^{2-} , Br⁻ and Cl⁻ only. Lead Pb(II) is challenging environment to calculate bond valence sum because of all bonds formed by Pb(II) not equal. The current study focuses on oxygen, bromine, and chlorine because it bonded with one type of atom (central atom) in a single crystal. This work use bond valence method to find bond valence sum and coordination number. The parameters (R_o , b) and observed bond length (R_{ij}) will apply in bond valence method equations, which obtain from www.iucrj.com only. Programs Crystal Maker, Origen, and Avogadro analyse the data and plot correlations.

1.5 Research Significance

This study is one of the studies that sought about the factors affecting the crystal form. The importance of this study is that it deals with the impacting electron lone pair on coordination number (CN), bond valence sum (BVS), bond distance (R). This work opens the door to clear understanding of the effect of electrons lone pair in the crystal.

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