Jurnal Kimia Valensi, Vol 5(2), November 2019, 211-217
Available online at Website: http://journal.uinjkt.ac.id/index.php/valensi

A Computational Study on the Effects of Molecular Structures of Di-n-butyldithiophosphate and of its Derivatives on the Stability of Their Complex Compounds with Rare-Earth Elements

Nurdeni[1], Atje Setiawan Abdullah[2], Budi Nurani Ruchjana[2], Hardianto A[3], Anggraeni A[3], Muthalib A[3], Husein H. Bahti[3,4]

[1]Mathematics education study program, , Faculty of Mathematics and Natural Sciences, University Indraprasta PGRI, Jakarta, Indonesia.
[2]Department of Mathematics, Faculty of Mathematics and Natural Sciences, Padjadjaran University, Jatinangor, Indonesia.
[3]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Padjadjaran University, Jatinangor, Indonesia.
[4]Central Laboratory, Padjadjaran University, Jatinangor, Indonesia.

Corresponding author: husein.bahti@unpad.ac.id.

Received: February 2019; Revision: March 2019; Accepted: November 2019; Available online: December 2019

Abstract

The stability of complex compounds formed from the ligand di-*n*-butyldithiophosphate (DBDTP) and its derivatives, with ions of rare-earth elements (REEs), such as gadolinium ion (Gd^{3+}), is an important factor in the separation and purification processes of the elements using solvent extraction method. The complex stability is dependent, one of which, on the partial charge of the donor atom (S atom in this case) in the molecule of DBDTP or its derivatives. The more negative the partial charge of the donor atom, the more stable is the complex compound formed. The purpose of this study is to explore the effect of electron donating, and of electron withdrawing groups, as well as the effect of the structure of the butyl group in the molecules of DBDTP and or its derivatives on the partial charge of the donor atom. The method used was the semi empirical quantum mechanical calculations, i.e. the Austin Model 1 (AM1). The results of the study showed that the electron withdrawing group of -CN had resulted in the most positive charge on the donor atom, if it is on the second carbon atom of the butyl group in the DBDTP and or its derivatives. Conversely, in the same carbon atom position, the donating electron group of $-CH=CH_2$ had generated the most negative partial charge on the donor atom. Furthermore, the results of this study also revealed that the *sec*-butyl isomer produced the most negative partial charge on the donor atom, among other isomers.

Keywords: Di-*n*-butyldithiophosphate derivatives, complex stability, partial charge, donor atom, Austin Model 1.

DOI:*10.15408/jkv.v5i2.10652*

1. INTRODUCTION

Rare-Earth Elements (REEs) are found in nature in the form of complex compounds, not as free elements or ions and thus, for their use, they must firstly be separated from their mixtures with other elements and compounds. Moreover, REEs are also usually found in their minerals in nature as mixtures of some different REEs. For example, the mineral monazite contains eight to ten different REEs to include lanthanum, cerium, neodymium, praseodymium, gadolinium, samarium, europium, terbium, and dysprosium. Thus, separation and purification processes are needed to obtain pure single elements, in order to be used for their particular applications.

Due to their unique nuclear, physical, and chemical properties, REEs have been used in high technology industries, such as refilled-batteries, fiber optics, detectors or sensors to diagnose diseases, and laser (Zhu *et al*., 2012). One particular REE, i.e. gadolinium, has been reacted with a particular ligand to form a complex compound, which is called a contrast agent to detect a desease by employing

P-ISSN: 2460-6065, E-ISSN: 2548-3013

Magnetic Resonance Imaging method (Fauzia *et al.*, 2017).

REEs are capable of forming stable complexes with phosphite- , carbamate- , and phosphate compounds as ligands, such as tributylphosphate (TBP). Based on this fact, TBP has been used to extract REEs (Ozturk *et al.*, 2010). Di-*n*-butyldithiocarbamate (DBDTC) and di-*n*-butyldithiophosphate (DBDTP) have been been used as complexing agents in reversed-phase liquid chronmatography of REEs. Individual La, Nd, Pr, and Ce has been successfully separated using DBDTC. Additionally, a good separation of Ce from La, Nd, or Pr using DBDTP has been reported (Bahti *et al.*, 2011). The DBDTP has also been applied to separate gadolinium from its mixture with samarium by batch solvent extraction (Sofyatin *et al.*, 2016). Unfortunately, the results of the study showed that the two elements were almost not separable. The reason for this is probably due to the very small different in distribution coefficients of the two elements, which is understood, considering the very close position of the two elements in the periodic table, and thus the very similar in their properties. In order to separate this particular mixture of REEs, other techniques of solvent extraction, such as counter-current extraction or some other more selective ligands should be used or developed.

The aim of this study was to find out a new ligand(s) which will be developed from DBDTP as the existing ligand, by making its derivatives and studying their complex stability using a computational method. Later, the new selected ligand(s) will be proofed through wet laboratory experiments whether they were not only to form stable complexes with REEs, but also they react with different REEs to form complexes having different solubilites, or different distribution coefficients, in an extraction system.

A ligand is an anion or a molecule having pairs of free electrons which can be donated to the central atom of its corresponding complex, or chelate (Suhartana, 2007). There are some properties of a ligand which can be optimize through its molecular design; they are: its total charge, the partial charge of donor atom, thermodynamic and kinetic stabiliy, lipophilicity, electronegativity, free (or lonely) electrons, molecular structure, and its inner shell solvation (Suhartana, 2007). It has been stated that the charge of donor atom, which may strongly contribute to the stability of a complex molecule, can be affected by its surounding electron donating and electron withdrawing groups (Suhartana, 2007). Different electron withdrawing and electron donating groups may cause differences in the structure, exitation energy of the complex, and the charge of electron pairs donating atom. Another report stated that a ligand with a longer alkyl group such as butyl, has a higher extraction efficiency than those with shorter alkyl groups (Setiawan, 2011).

Based on the theoretical basis given above, the effect of electron donating and of electron withdrawing groups, as well as the effect of the structure butyl group, on the charge of electron pairs donating atom in the complex of Gd(III)-DBDTP and of Gd- (III)-DBDTP derivatives, have been studied.

Talking about chemical computation which is used in this study, it will be mentioned that as the technology develops, chemical computation also develops very fast, especially in its application in help designing, theoretical study, and *in silico* molecular modelling. This study was carried out by using theoretical chemisty and experiments which have been translated into computer programs, to calculate molecular properties and their changes, and to do simulations on molecular systems, which can be applied to the real chemistry (Prianto, 2010). The simulations which have been done were to design DBDTP derivatives , and to calculate the partial charges of the donor atom of DBDTP.

Published reports on partial charge of the donor atom varied from very bad to very good. Although a big number of different methods to determine partial charge of the donor atom from the quantum chemistry calculation have been proposed during several decades, many of the proposed methods were not able to handle various types of material (Manz and Limas, 2016); (Limas and Manz, 2016).

So far, the method used to calculate the charge of donor atom is the semi empirical quantum mechanics, i.e. the Austin Model 1 (the AMI) method. This method has been chosen a lot, because the parameter calculated is only electron valency of the atoms, so the analysis time is relatively short without lowering the acuracy of calculations. In addition, the quantum mechanic calculations

using the AMI method is able to give accurate calculation results on physical chemistry properties of the structure of a molecule. For example, the AMI method is able to predict electronic properties such as the charge of an atom, polarizability, dipole moment, partition coefficient, molar volume, Chemical Schiff constant on NMR, which can be applied to non-standard systems (Anjar Purba Asmara, 2015). Apart from this, the semi empirical AMI method is capable of selecting functional monomers which are effective to synthesize printed polimer diazinone, in order to increase the selectivity and affinity of the QCM sensor (Saputra *at al.,* 2013). Another advantage of this method is the possibility of calculating the properties of complex molecules, and the calculation results are significantly correlated with the results of experiments (Ananto, 2017). This present study is hoped to be able to give illustrations on the suitable substituents in designing good DBDTP derivatives.

2. MATERIALS AND METHODS

Materials and Instruments

The material used in this study was the figure of molecular structure of di-*n*-butyldithiophosphate (DBDTP) as the existing ligand. The instrumnets used in the experiments consisted of hardwares and soft-wares. The hard-wares were a laptop with a processor of Intel (R) Core (TM) i5-5200U CPU @2,20 GHz 980, Memory RAM 8GB, 64-bit operating system, x64-based processor, Hardisk 2 TB. The soft-wares used were Amber14, AmberTools 15, Discovery Studio 2016, Geany, and the Linux Operating System.

Modelling and Preparation of Molecular Structures of Gadolinium (II) Complex with DBDTP.

The 2D structure of DBDTP and of its derivatives were firstly modelled using the BIOVIA draw 2016. The resulted 2D structures of the ligands were then converted into their 3D structures using the BIOVIA Discovery Studio 2016 program. This was followed by energy optimization through geometry cleaning. As electron donating groups, $-CH_3$, $-CH=CH_2$, and -OH groups have been selected for the investigation in this work. Meanwhile, the functional groups of $-CF_3$, -CN, -COH, and $-NO_2$ have been selected for experiments on the effects of electron withdrawing groups. The resulted models of DBDTP were then put in the pdb file formate.

Calculation of the Charge of Atoms in DBDTP Molecule and in Its Derivatives Using The Semi Empirical AMI Method

Semi empirical calculations using the AMI method were carried out after all of the DBDTP derivatives modified with the studied groups of electrons withdrawing- and of electrons donating, were put in the form of pdb. The calculation results of partial charge of the atoms were presented using the Amber 14 and Amber Tools 15 programs. This was followed by conversion of pdb into mol2.

3. RESULTS AND DISCUSSIONS

Optimization of the Geometry of Gd(III)-DBDTP Complex Compound

The first step was to design the complex compound of Gd (III) with the ligand DBDTP, which was followed by calculating the partial charge of the sulphur (S) atom using the Amber14 dan Amber Tools 15 programs. The results of the calculations were then put in mol2. These results of calculations using the semi empirical AMI method showed that the partial charge of S atom had a partial charge of –1.2530, before be given any of electron withdrawing and of electron donating groups. The molecular structure of DBDTP is presented in Figure 1.

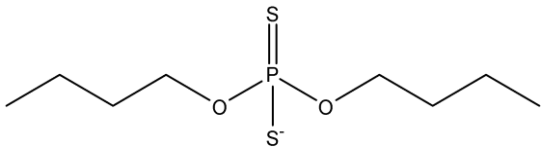


Figure 1. Molecular structure of di-*n*-butyldithiophosphate (DBDTP).

The charge of S atom in the dithiophosphate functional group of DBDTP, which directly interacts with gadolinium as the central atom, may have its effect on the stability of the complex compound formed between DBDTP and gadolinium. There are some factors determining the stability of the complex compound, two of them are the central atom (i.e. the metal) and the ligand (Suhartana, 2007).

Results of Semi Empirical AMI Calculations of The Partial Charge of S Atom in DBDTP Derivatives

After designing the molecules of DBDTP derivatives having electron withdrawing and or electron donating groups, the experiments were continued by calculations of the partial charge of S atom in each molecule of the DBDTP derivatives. Results of the calculations are presented in Table 1 and Table 2.

The resulted data in Table 1 showed that from the four groups of electron withdrawing studied (i.e. $-CF_3$, -CN, -COOH, and $-NO_2$), the – CN group at position C_2 of the butyl chain (R_2) gave the biggest increase in the partial charge of S atom; from – 1.2530 in DBDTP to -1.2625 in the corresponding DBDTP derivative. The partial charge of an atom can be used to determine the ionic bond level *versus* covalent bond of any element on the Periodic Table. The need for such a quantity appears, for example in molecular simulation to calculate bulk and surface properties which are in agreement with the results of experiments.

The resulted data in Table 2 showed that from the three groups of electron donating studied (i.e. $-CH_3$, $-CH=CH_2$, and -OH), the $-CH=CH_2$ group at position C_2 of the butyl chain (R_2) gave the biggest increase in the partial charge of S atom; from – 1.2530 in DBDTP to -1.268 5 in the corresponding DBDTP derivative.

From the above two tables it can be concluded that electron donating groups, such as $-CH=CH_2$, had increased the negative charge of the S atom as an electron donor to make a stronger bond with the metal atom. Conversely, electron withdrawing groups, such as –CN, had decreased the negative charge of the S atom as an electron donor. These results are usefull to design a ligand to form a complex compound with a particular rare-earth element. Metalic ions have different radii and charge, and thus ligands of suitable character are required to form stable complexes.

The Effects of Molecular Structure of Butyl Grooup in The DBDTP Derivatives

The butyl group in the molecules of the DBDTP, which was derivatized, has its molecular structure of *n*(normal)-butyl-, whereas in the three DBDTP derivatives, the butyl group may take the forms of *sec*-butyl, *iso*-butyl-, and tertier) butyl-. In this study, the effect of each of the three different structures of butyl group, on the partial charge of S atom, has been studied. The studied parameters included molecular structure of the butyl group and the charge of S atom in DBDTP and of its derivatives.

Table 1. Calculation results of the effect of electron withdrawing groups on the charge of atom (S) in the DBDTP derivatives.

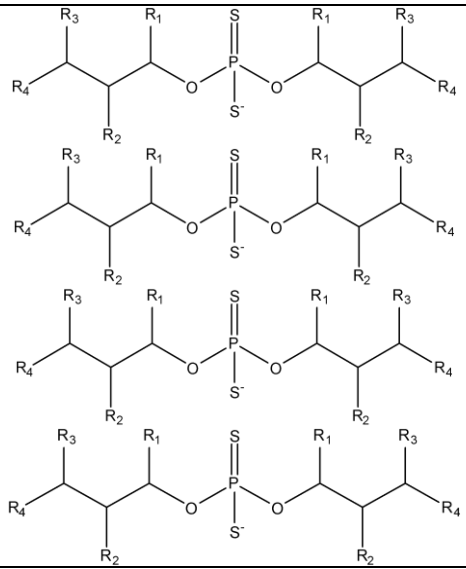
General Molecular Structure of DBDTP Derivatives	Electron Withdrawing Group	The Charge of Donor Atom (S)
	$R_1 = CF_3$	-1.2130
	$R_2 = CF_3$	-1.2445
	$R_3 = CF_3$	-1.2390
	$R_4 = CF_3$	-1.2455
	$R_1 = CN$	-1.2190
	$R_2 = CN$	-1.2625
	$R_3 = CN$	-1.2495
	$R_4 = CN$	-1.2495
	$R_1 = COOH$	-1.2430
	$R_2 = COOH$	-1.2440
	$R_3 = COOH$	-1.2455
	$R_4 = COOH$	-1.2440
	$R_1 = NO_2$	-1.1745
	$R_2 = NO_2$	-1.2265
	$R_3 = NO_2$	-1.2500
	$R_4 = NO_2$	-1.2600

Table 2. Calculation results of the effect of electron donating groups on the charge of atom (S) in the DBDTP derivatives.

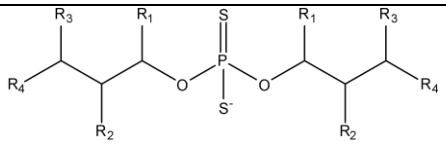
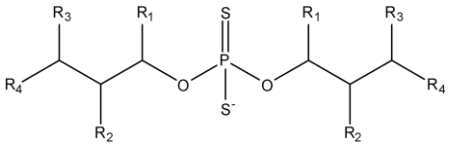
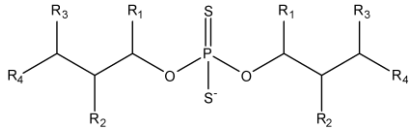
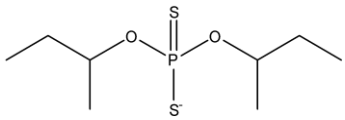
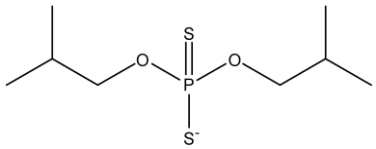
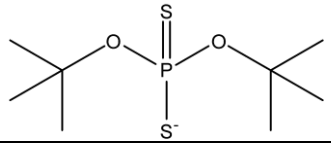
General Molecular Structure of DBDTP Derivatives	Electron Donating Group	The Partial Charge of Donor Atom (S)
	$R_1 = CH_3$	-1.2570
	$R_2 = CH_3$	-1.2495
	$R_3 = CH_3$	-1.2530
	$R_4 = CH_3$	-1.2500
	$R_1 = CH{=}CH_2$	-1.2510
	$R_2 = CH{=}CH_2$	-1.2685
	$R_3 = CH{=}CH_2$	-1.2490
	$R_4 = CH{=}CH_2$	-1.2490
	$R_1 = OH$	-1.2665
	$R_2 = OH$	-1.2570
	$R_3 = OH$	-1.2665
	$R_4 = OH$	-1.2480

Table 3. Calculation results of the effect of different butyl isomers on the partial charge of donor atom (S) in the DBDTP derivatives.

Number	DBDTP Derivatives with The Different Butyl Isomer	Name of Butyl Isomer	The Partial Charge of Donor Atom (S)
(1)		*sec*- butyl	-1.2960
(2)		*iso*-butyl	-1.2520
(3)		*t*-butyl	-1.2940

The parameters have been theoretically studied by using molecular designing with energy optimization, followed by molecular dynamic and calculations using the semi empirical AMI method. Results of the calculations are presented in Table 3. The resulted data in Table 3 showed that *sec*-butyl group gave a bigger increase in the partial charge of S atom ((-1.2960) than its original value in *n*-butyldithiophosphate (–1.2530, see section 3a above) and from the others DBDTP derivatives.

4. CONCLUSION

From the discussions given above it can be concluded that electron donating groups in the molecule of DBDTP derivatives increased the charge of donating (S) atom, with the biggest value was given by the $–CH_2{=}CH_2$ at the position C_2 of the butyl group. Whereas, electron withdrawing groups in the molecule of DBDTP derivatives decreased the charge of donating (S) atom, with the biggest value was given by the –CN group, also at the position C_2 of the butyl group. The study on the effect of molecular structure of the butyl group in DBDTP, resulted in data showing that the *sec*-butyl group gave a bigger increase in the partial charge of S atom than its original value in *n*-butyldithiophosphate and in the two other DBDTP of different butyl isomers. Moreover, it can be be concluded that the

stability of complex compounds formed between the ligand dibutyldithiophosphates of different isomers of butyl group, with the rare-earth element ion [(Gd(III)] is dependent on the presence of electron donating- and of electron withdrawing groups, as well as on the molecular structure of the butyl isomer in DBDTP molecule.

The results of this present study is hoped to be able to be used as a guide in synthesizing DBDTP derivatives by wet laboratory experiments.

ACKNOWLEDGEMENTS

I would like to thank the Ministry of Research, Technology, and Higher Education for Supporting the authors with fund, through the BPPDN scholarship (2014-2017) and the research grant for Doctoral Dissertation Research (2018).

The authors would like to thank to all the people in that have given their supports and contributions to the success of this research work. They are the Rector of University Indraprasta PGRI and of Padjadjaran University, the dean of the Faculty of Mathematics and Natural Sciences of Unpad, the dean of the Faculty of Mathematics and Natural Sciences of UNINDRA, and the head of Department of Chemistry, Unpad, and the head of mathematics education study program, UNINDRA, and others who will not be mentioned here, one by one.

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