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STABILITY OF COORDINATION COMPOUNDS OBTAINED BY REDUCTION OF COPPER(II) HALIDE AND 1,3–BIS(DIPHENYLPHOSPHINO)PROPANE (DPPP)

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ABSTRACT

1,3–Bis(diphenylphosphino)propane (dppp) and copper(I) halide form in chloroform a dimeric coordination compound [(dppp–P,P)Cu(μ–X)$_2$Cu(dppp–P,P')]. A coordination compound of copper(II) halide with dppp has never been synthesized. However, reduction of copper(II) to copper(I) may occur during the synthesis. The present investigation is focused on the reduction of copper(II) to copper(I) in the course of the reaction of CuX_2 (X = Cl, Br) and dppp of 1:1 mole ratio in acetone. The synthesis conducted produces M ($CuCl_2$ and dppp) and N ($CuBr_2$ and dppp). They are colorless prism and needle crystals and have a melting point in the ranges of 82°C - 84°C and 165°C - 167°C, respectively. The free energy of M compound is –11711,9383 kJ mol^{-1}, while that of N compund is –14507,58 kJ mol^{-1}. Halide ion qualitative and electrical conductivity tests show that M compound is molecular, while N compound is an ionic one. The predicted chemical formulas of M and N compounds are [(dppp-P,P')Cu(μ-Cl)$_2$Cu(dppp-P,P')] and [Cu(μ–dppp)$_2$Cu(μ–dppp)]$_n$.2nBr Although the result differs from what was expected, both coordination compounds are obtained in the course of reduction of copper(II) to copper(I).

Keywords: *synthesis, coordination compound, copper(II) halide,1,3–bis(diphenylphosphino)propane.*

INTRODUCTION

The interaction of 1,3–bis(diphenylphosphino) propane (dppp) and copper(I) halide in chloroform is described [6] to form a dimeric coordination compound [(dppp–P,P')Cu(μ–X)$_2$Cu(dppp–P,P')]. Distorted tetrahedral geometry of Cu(I)is reported. Coordination compounds of copper(II) halide and dppp have never been synthesized in acetone. Copper(II) halide is found [5] able to form, using the same salts, a coordination compound with the monodentate ligand containing a P donor atom, triphenylphosphine (PPh_3). Thus [$CuCl_2(PPh_3)_2$] of Cu(II) square geometry is the only coordination compound which has been synthesized.

Meanwhile the coordination compounds of copper(II) halide with dppp are expected to have a different structure when compared to that of [(dppp–P,P') Cu(μ–Br)$_2$Cu(dppp–P,P')] because the size of copper(II) is smaller than that of copper(I). However, reduction of copper(II) to copper(I) may occurs during the synthesis. The purpose of this research is to determine and characterize the stability of the predicted structure of synthesized in acetone compounds of CuX_2 (X= Cl, Br) and dppp. The structure considered may verify the possiblity of copper(II) reduction to copper(I) in the course of such coordibation compounds synthesis.

EXPERIMENTAL

$CuCl_2.2H_2O$ (Merck Index, p.a), $CuBr_2$ anhydrate (Merck Index, p.a), dppp (Disperc Chemicals, p.a), $AgNO_3$ (Merck Index, p.a), and acetone (Sigma Aldrich, p.a) were used as purchased. The method of synthesis was adapted on the groundof the method of synthesis of 1,3-bis (diphenylphosphino)propane (dppp) and copper(I) halide [6]. It is worth adding that the synthesis used acetone as a solvent. The coordination compound was synthesized by adding an acetone (5 ml) solution of $CuCl_2.2H_2O$ ($2{,}04x10^{-2}$ g; $12x10^{-2}$ mmol) to an acetone (5 ml) solution of dppp ($5x10^{-2}$ g; $12x10^{-2}$ mmol). The mixture of these two solutions was stirred in an ultrasonic water bath at 30˚C for 60 min. The solution obtained was subjected to a slow evaporation by covering with an aluminium foil and subsequent crystallization.

Following the same steps, an acetone (3 ml) solution of anhydrous $CuBr_2$ ($2{,}68x10^{-2}$ g; $12x10^{-2}$ mmol) was poured into an acetone (3 ml) solution of dppp ($4{,}91x10^{-2}$ g; $12x10^{-2}$ mmol). The mixture of these two solutions was stirred in an ultrasonic water bath at 30˚C for 45 min. The solution obtained was subjected to a slow evaporation by covering with an aluminium foil and subsequent crystallization.

Melting point determination of the synthesis products gave information on the coordination compounds novelty, purity, and thermal stability. Electrical conductivity and qualitative halide ion test (by reacting with $AgNO_3$) were carried out to determine whether the compound formed was molecular or ionic one. SEM–EDX analysis was conducted to determine the to determine the elementals composition and their percentage of the coordination compounds which in turn provided the elucidation of their empirical formula. The chemical formula of the compound was determined on the ground of the empirical formula, qualitative halide ion and electrical conductivity test results. It in turn was used to predict the compound structure. The free energy of the latter was calculated by SPARTAN '14.V1.1.0 program.

RESULTS AND DISCUSSION

The mixing of $CuCl_2$ solution with dppp gives a yellowish to a colorless mixture, while that obtained by mixing $CuBr_2$ solution with dppp looked brownish to colorless. These findings indicate a possibility of copper(II) halide reduction to copper(I) halide described below:

$$\begin{array}{lcl} \text{Reduction: } e^- + Cu^{2+}_{(aq)} & \rightarrow & Cu^+_{(aq)} \\ \text{Oxidation: } 2X^-_{(aq)} & \rightarrow & X_{2(aq)} + 2e^- \\ \hline 2CuX_{2(aq)} & \rightarrow & Cu_2X_{2(aq)} + X_{2(aq)} \end{array}$$

This possibility is also supported by the synthesis results. M compound (the product of $CuCl_2$ and dppp interaction) is obtained in the form of colorless prism crystals, while N compound (the product of of $CuBr_2$ and dppp interaction) is obtained in the form of colorless needle crystals. They are shown in Fig. 1.

The results of the melting point test are shown in Table 1. These data shows that the coordination compounds are new and pure, as the melting point is found between the melting points of the reagents.

The results of the electrical conductivity are listed in Table 2. They provide the prediction that M and N compounds have a molecular and an ionic coordina-

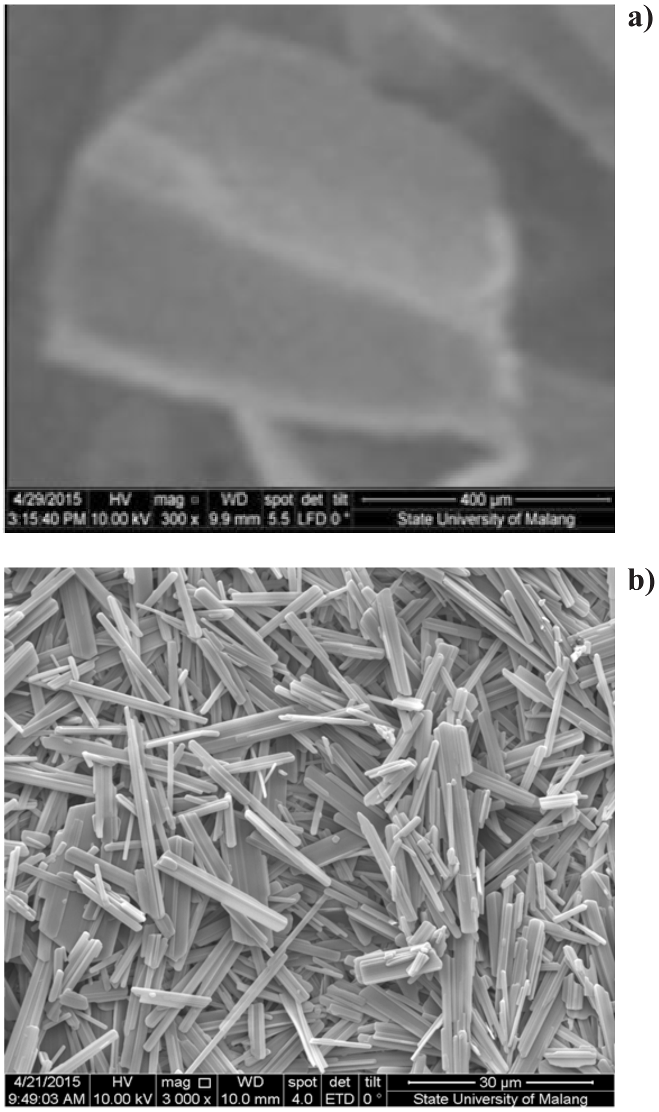

Fig. 1. Results of SEM analysis: Crystal structure of M Compound (a) and N Compund (b).

Table 1. Melting point data.

Sample	Melting Point (˚C)
M Compound	82–84
N Compound	165–167
$CuCl_2.2H_2O$	100 (Merck Index)
$CuBr_2$ anhidrate	498 (Merck Index*)*
Dppp	63–65 (Disperc Chemicals Index)

Table 2. Electrical conductivity data.

Sample Solution	Concentration (M)	Electrical Conductivity (μS/cm)
M compound	0,0029	3,94
$CuCl_2.2H_2O$	0,0029	88,6
N Compound	0,03	141,70
$CuBr_2$ anhidrate	0,03	115,90
Acetone	–	3,92

tion, respectively. Even though the synthesis described uses the same ligand and the same solvent, the results are different.

Table 3. Elementals composition of M Compound.

Element	Percentage of Atom (*%At*)	Percentage of Massa (*%Wt*)
C	80,77	60,20
P	6,11	11,75
Cu	3,87	15,27
Cl	2,99	6,57

The qualitative halide ion test carried out shows that the interaction of M compound does not give a white precipitate of AgCl, while that of N compound produces a brownish yellow of precipitate of AgBr. These results indicate that the chloride ion of M compound acts as a ligand, while the bromide ion of the N compound acts as a counterweight ion. These results support those of the electrical conductivity test.

EDX analysis results referring to M compound are shown in Fig. 2.

The elemental composition derived is presented in Table 3. It leads to $C_{27}H_{26}ClCuP_2$ as the empirical formula of M coordination compound.

The EDX results referring to N compound are shown in Fig. 3.

The elemental composition derived is presented in Table 4. It leads to $C_{81}H_{78}Br_2Cu_2P_6$ as the empirical formula of N coordination compound.

It is worth stating that both empirical formulas in-

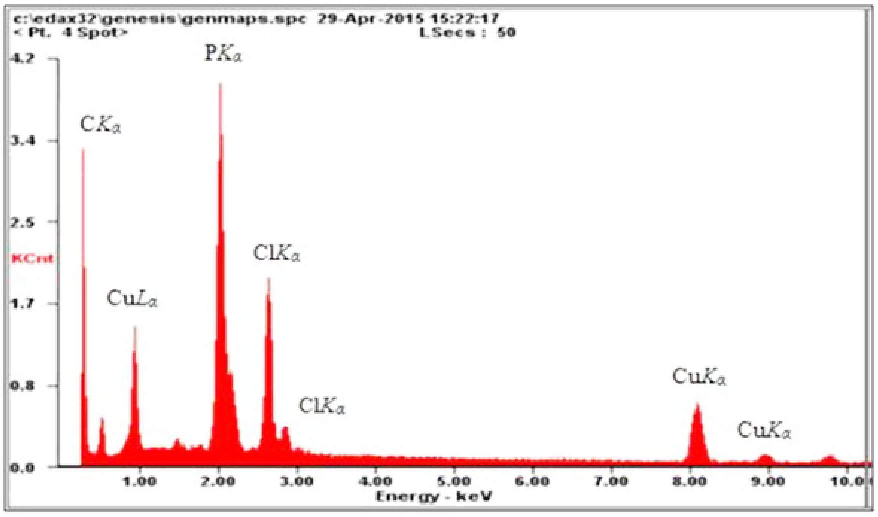

Fig. 2. EDX results referring to M Compound.

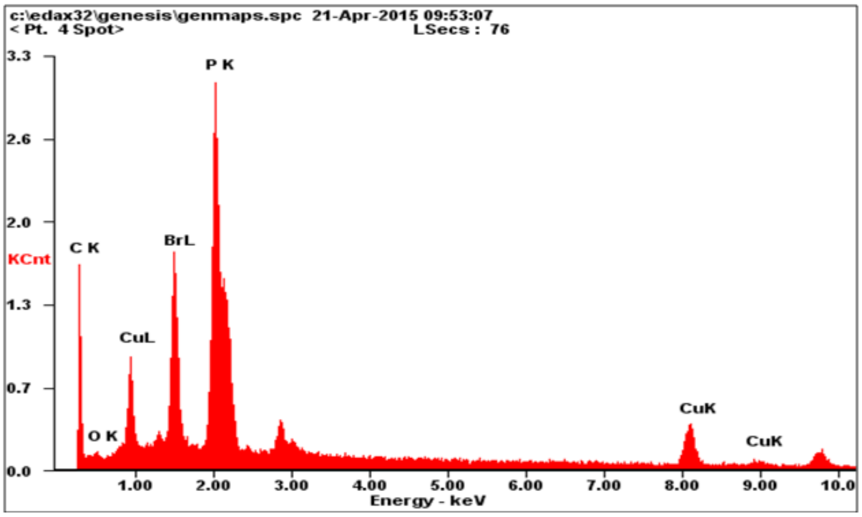

Fig. 3. EDX results referring to N Compound.

Table 4. Elementals Composition of N Compound.

Element	Percentage of Atom (*%At*)	Percentage of Massa (*%Wt*)
C	80,32	51,75
`P	10,34	17,18
Cu	3,32	11,30
Br	4,26	18,26

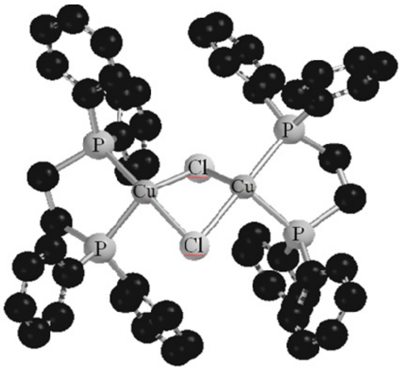

Fig. 4. M compound structure model.

dicate reduction of copper(II) to copper(I) in the course of the synthesis.

The coordination compounds of copper(II) have coordination numbers ranging from 4 to 8 [2, 3, 5, 9]. Furthermore, dppp is generally found in a coodination compound as a bidentate chelate ligand [1, 4, 6]. In view of these findings and the results of the compounds characterization, it is suggested that M compound has the chemical formula of the coordination compound [(dppp-P,P′)Cu(μ-Cl)$_2$Cu(dppp-P,P′)] [6]. The chloride in M compound acts as a bridging ligand, while dppp acts as a bidentate chelate ligand. Cu(I) geometry is distorted tetrahedral. The free energy of this compound is –11.711,9383 kJ mol^{-1} in accord with the results of SPARTAN'14.V1.1.0 program application. The structure model of M compound is shown in Fig. 4.

This N compound case differs. It might be either an ionic dimer or an ionic polymer. [(dppp–P,P') Cu(μ–Br)(μ–dppp)Cu(dppp–P,P')].Br is the chemical formula of the ionic dimer with a tetrahedral Cu(I) geometry. [Cu(μ–dppp)$_2$Cu(μ–dppp)]$_n$.2nBr is the chemical formula of the ionic polymer with a trigonal planar Cu(I)geometry. Based on the results of SPARTAN'14.V1.1.0 optimization, the free energy of ionic dimer is –9.866,07 kJ mol^{-1}, while that of the ionic polymer is –14.507,58 kJ mol^{-1}. The structures of the coordination compound are illustrated in Fig. 5.

One of dppp in the ionic dimer compound acts as a bridging ligand, while the two other act as a bidentate chelate ligand. In the ionic polymer compound, dppp acts as a bridging ligand. The center atom of the ionic dimer compound, Cu (I), has a coordination number of 4, while the geometry around the atom is distorted tetrahedral. The center atom of the ionic polymer compound, Cu (I), has a coordination number of 3, while the geometry around the atom is trigonal planar.

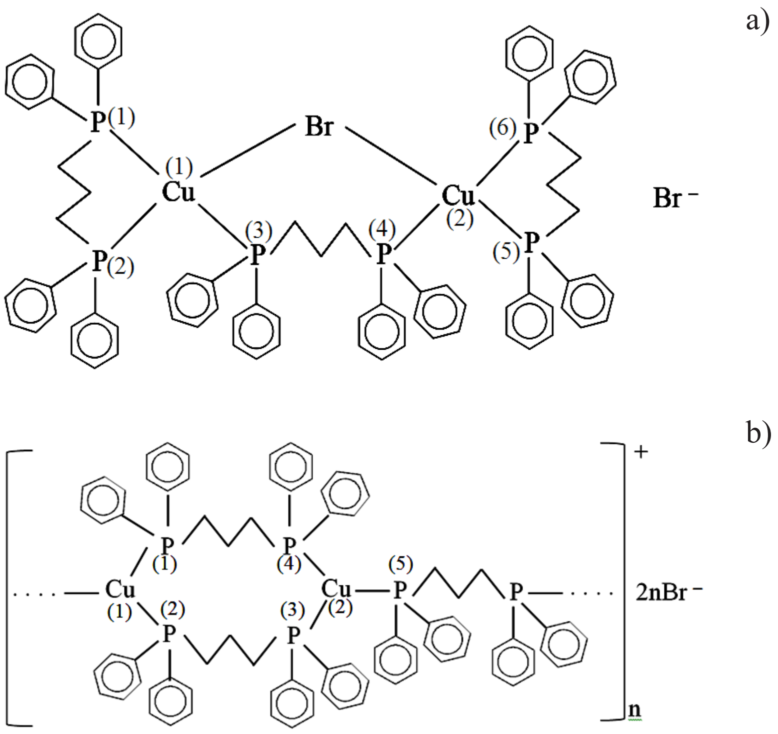

Fig. 5. A modeling structures of N compound: (a) [(dppp–P,P')Cu(μ–Br)(μ–dppp)Cu(dppp–P,P')]Br; (b) [Cu(μ–dppp)2Cu(μ–dppp)]n.2nBr.

The structure of ionic dimer compound is stabilized by a chelate but its ligands repulsion is greater than that of the ionic polymer. Besides, the latter structure is not stabilized by a chelate. The stabilization effect of the chelate could be considered lower than that of the repulsion between the ligands. That is why the polymer ionic structure is more stable and has a lower free energy than that of the ionic dimer.

The ionic polymer structure has different long bondings of Cu–P with $[Cu(PPh_3)_2Br]$ even though it has a coordination number of 3 [7]. The different values of Cu–P long bonding are shown in Table 5.

The long bonding of the ionic polymer Cu(2)–P(5) in $[Cu(\mu\text{–dppp})_2Cu(\mu\text{–dppp})]_n.2nBr$ is shorter than the other Cu–P bondings. It is so because Cu(2)–P(5) bonding is not a part of the ring structure. The latter causes a ring strain which can lead to stability decrease, i.e. stability is reached with ring strain decrease. In fact, the decrease of the ring strain results from increase of the long Cu–P bonding. That is why those involved in the ring structure are longer than Cu(2)–P(5) long bonding.

Even though both structures have a coordination number of 3, the average value of Cu–P long bondings in the polymer ionic compound is higher than that of $[Cu(PPh_3)_2Br]$. This is due to the ring strain in the polymer ionic compound, which can decrease with increase of the long bonding.

Table 5. Long bonding of Cu–P of $[Cu(\mu\text{–dppp})_2Cu(\mu\text{–dppp})]_n.2nBr$ and $[Cu(PPh_3)_2Br]$.

$[Cu(\mu\text{–dppp})_2Cu(\mu\text{–dppp})]_n.2nBr$		$[Cu(PPh_3)_2Br]$	
Bonding	Long Bonding (Å)	Bonding	Long Bonding (Å)
Cu(1)–P(1)	2,413	Cu–P	2,262
Cu(1)–P(2)	2,420		
Cu(2)–P(3)	2,412		
Cu(2)–P(4)	2,415		
Cu(2)–P(5)	2,405		
Average of Cu–P	2,413		

The structures predicted so far are not accurate. X–ray diffraction analysis of single crystals is required to get a more precise picture. It is still not clear why using identical solvent and salt one gets different products of the synthesis carried out.

CONCLUSIONS

A reaction between CuX2 (X = Cl, Br) and dppp of an stoichiometric ratio of 1:1 took place in acetone. It was connected with reduction of copper(II) to copper(I). $CuCl_2$ and dppp formed a molecular dimer compound of the chemical formula $[(dppp\text{-}P,P')Cu(\mu\text{-}Cl)_2Cu(dppp\text{-}P,P')]$, while $CuBr_2$ and dppp formed an ionic polymer compound of the most possible chemical formula $[Cu(\mu\text{–}dppp)_2Cu(\mu\text{–}dppp)]_n.2nBr$.

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