*Full Length Research Paper*

# Kinetic, mechanism and spectral studies of bis (dibenzoyl-methane) copper (II) complex and its adducts

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The copper (II) complex of 1, 3-diphenyl-1, 3-propanedione (dbm) and its adducts with 2, 2-bipyridine (bipy) and 1, 10-phenantroline (phen) were synthesized. They were characterized by micro analytical data, infrared and ultraviolet (UV)-visible spectra and magnetic susceptibility data. The kinetics of the formation of the complex follows a rapid pre-equilibrium in which the rate is independent of the metal concentration, suggesting an interchange associative mechanism.

**Key words:** Copper (II)-adducts, kinetics, mechanism of formation, interchange associative mechanism.

## INTRODUCTION

β-dicarbonyl compounds are very versatile ligands. They exhibit various bonding modes to metal ions (Stephen, 1989). Copper (II) complexes and adducts play important roles in both synthetic and structural research because of their preparative accessibility, structural diversity (Ahmed et al., 2007; Aliyu and Sanni, 2008) and biological activities (Patel et al., 2008; Shalin and Saxena, 2009). Various complexes involving copper II ions and β-dicarbornyl compounds have been synthesized and characterized (Ahmed et al., 2007; Patel, 2009; Sylvester, 2006). Studies show that the commonest types of diketonate complexes are those with stoichiometries: [M -(β-dike)$_3$] and [M- (β-dike)$_2$] (Sylvester, 2006). Bis-(β-diketonato) metal (II) complex behaves as Lewis acid and forms five or six coordinate adducts with neutral donor molecules (Harding et al., 2010). The kinetics and mechanism of the reaction of Cu (II) with pentane-2,4-dione and 4, 4, 4.-trifluoro-1-(2-thienyl) butane-1, 3-dione

have been investigated by different authors. It was reported that the keto form of pentane-2, 4-dione reacts with Cu (II) at an abnormally slow rate. Complex formation was proposed to occur via a precursor complex in which the metal ion is loosely bound to the protonated keto tautomer.

The rate of the reaction was 2 x 10$^4$dm$^3$ mol$^{-1}$s$^{-1}$. As a comparison, the solvent exchange rate for Cu (II) amounts to 1x10$^9$dm$^3$ mol$^{-1}$s$^{-1}$ (Hugee et al., 1993). In another study, it was further asserted that rapid reactions such as those involving the formation of complexes of Cu (II) are likely to be affected by steric factors (Micheal and Brigid, 1979). Sterically, square planar complexes are less favored, but with large, bulky ligands, steric hindrance may prevent additional ligands from co-ordinating to the metal. Dibenzoylmethane (1,3-diphenyl-1,3-propanedione,dbm) has been used as chelate "blocking" ligand due to the bulky phenyl groups which reduce packing efficiency, providing opportunities for solvated structures. In [Cu (dbm)$_2$], the Cu (II) atom is located on a symmetry centre and is surrounded by four O atoms from two dbm molecules forming a plane-square coordination environment. The aims of this work are (i) to

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**Table 1.** Analytical data of the [Cu (dbm)$_2$(H$_2$O)$_2$] complex and its –bipy and phen adducts.

| Compound | Molecular formula | Formula mass | Colour | Yield (%) | Melting point (°C) | Analysis; found (Calc.) (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Cu | C | H |
| Cu (dbm)$_2$. (H$_2$O)$_2$ | Cu[C$_6$H$_5$COCH$_2$COC$_6$H$_5$]$_2$ 2H$_2$O | 546.092 | Green | 60 | 270 | 11.54 (11.64) | 65.46 (65.98) | 4.61 (4.29) |
| Cu (dbm)$_2$ phen | Cu[C$_6$H$_5$COCH$_2$COC$_6$H$_5$]$_2$ C$_{12}$H$_8$N$_2$) | 710.22 | Green | 46 | 220 | 6. 17 (6.05) | 76.01 (75.45) | 4.48 (4.41) |
| Cu(dbm)$_2$ bipy | Cu[C$_6$H$_5$COCHCOC$_6$H$_5$]$_2$ (C$_{10}$H$_8$N$_2$) | 666.242 | Green | 50 | 230 | 9.87 (9.54) | 72.20 (72.11) | 4.54 (4.53) |

**Table 2.** Infrared bands for the ligand, complex and adducts (cm$^{-1}$).

| Compound | Y $_{c-o}$ | Y $_{C=O+C=C}$ | Y $_{Cu-N}$ | Y $_{Cu-o}$ |
|---|---|---|---|---|
| dbm | 1228 | 1596 | - | - |
| [Cu(dbm)$_2$(H$_2$O)$_2$] | 1218 | 1542 | - | 548 |
| [Cu(dbm)$_2$phen] | 1231 | 1593 | 570 | 548 |
| [Cu(dbm)$_2$bipy] | 1231 | 1593 | 570 | 548 |

prepare [Cu (dbm) $_2$(H$_2$O)$_2$], (ii) to react it with 2, 2-bipyridine (bipy) and 1, 10-phenantroline (phen) to form adducts,(iii) to determine the kinetic of formation of [Cu(dbm)$_2$(H$_2$O)$_2$] in view of exploring the mechanism of reactions and (iv) to use the proposed mechanism alongside spectroscopic data to suggest the formula of the probable intermediates.

## MATERIALS AND METHODS

### Synthesis

#### Preparation of the Cu(II) complex with dbm

2.99 g (0.015 moles) of Cu (II) acetate monohydrate in 100 cm$^3$ of aqueous methanol was reacted with 6.72 g (0.03 moles) of 1,3-diphenyl-1,3, propanedione in 20 cm$^3$ of methanol on a magnetic stirrer. Precipitation occurred immediately, and the resulting compound was washed with water and aqueous methanol before drying in a desicator over anhydrous calcium chloride

#### Preparation of the bipy and phen adducts

0.77 g (0.0040 moles) of the solid complex was added gradually to 1.00 g (0.0066 moles) of bipy in 25 cm$^3$ of chloroform on a magnetic hot plate stirrer at 70°C. This was stirred for about 1 h before filtering by suction; the collected adduct was then dried in a desiccator over silica gel. The phen adduct was similarly prepared.

#### Electronic absorption spectra

The electronic spectra of the complex and adducts were measured in aqueous methanol on a Lambda 3B ultraviolet (UV)/Visible spectrophotometer at 298 K.

#### Infra red spectra

The infrared spectra of the complex and adducts were recorded between 400 to 4000 cm$^{-1}$ on a Nicolet Aviatar 330 Fourier Transform InfraRed (FT-IR) spectrophotometer using KBr discs.

#### Kinetic measurements

Kinetic measurements were carried out in thermostated water bath at 298K. Solutions of aqueous methanol in large excess of metal (10$^{-3}$M) to ligand (10$^{-5}$M) were mixed together to ensure pseudo-first order kinetic runs at various concentrations. This was done on a Lambda 3B UV/Visible spectrophotometer at 259 nm.

## RESULTS AND DISCUSSION

### Elemental analysis

The results of the C, H and metal analysis show that the copper-dbm complex was formed with 1:2 metal: ligand ratio as expected for divalent metal complexes and from the crystal structure (Table 1).

### Infrared spectra

Table 2 reports the IR bands for the ligand, complex and adducts. The cis-enol form of β-diketones are characterized by strong intramolecular hydrogen bond (Tayyari et al., 2007).

Thus, a weak but broad band at 3442 cm$^{-1}$ is attributed to enolic OH stretch. On chelation, the only band in this

**Table 3.** Observed rate const *(k$_{obs}$),* at varied concentration of Cu (II) at 298 K.

| [DBM] x 10$^{-6}$M | [Cu$^{2+}$ x 10$^{-3}$M] | | | |
|---|---|---|---|---|
| | 1.0 | 1.5 | 2.0 | 2.5 |
| | k$_{obs}$ | k$_{obs}$ | k$_{obs}$ | k$_{obs}$ |
| 0.625 | 0.0122 ±0.004 | 0.0322±0.001 | 0.0420±0.002 | 0.0408±0.004 |
| 1.250 | 0.0219±0.003 | 0.0361±0.002 | 0.0447±0.004 | 0.0480±0.003 |
| 2.500 | 0.0322±0.001 | 0.0407±0.003 | 0.0465±0.001 | 0.0520±0.002 |
| 5.000 | 0.0376±0.002 | 0.0420±0.002 | 0.0479±0.003 | 0.0550±0.001 |
| 10.000 | 0.0509±0.001 | 0.0450±0.002 | 0.0502±0.001 | 0.0575±0.002 |

region is strong and sharp at 3021cm$^{-1}$which could be attributed to H$_2$O. There was virtually no absorption in this region in the adducts. The characteristic Y$_{c=o+}$ Y$_{-c=c}$ bands of dbm appear at 1596 cm$^{-1}$,insertion of Cu (II) lowers it to 1542 cm$^{-1}$ in the bis complex, while it appears at 1593 cm$^{-1}$ in the phen and bipy adducts, respectively.

Agwara et al. (2010) ascribe such bands to ring vibrations of uncoordinated bipy and phen at 1588 cm$^{-1}$. Similar band observed in the spectra of dibenzoylmethane and benzoylacetone at 1600 cm$^{-1}$ was assigned to aromatic stretching vibration (Aliyu and Mustapha, 2009). The bands at 570 cm$^{-1}$ and 548 cm$^{-1}$ are assigned to Cu-N and Cu-O, respectively; similar assignments were made by Rahmam et al. (2010) and Agwara et al. (2010).

## Electronic spectra

Dibenzoylmethane in methanolic media showed three intense bands at 205, 262 and 349 nm, which are assigned to π-π* and n-π* transitions (Prasad et al., 2007). The copper (II) ion gave a single broad band at 973 nm. On complexation, peaks due to the ligand appeared as a single sharp band at 241 nm. This confirms the involvement of diketonate oxygen atoms in bonding (Sakar et al., 2008) the band resulting from d-d transition shifted to 976 nm, in the dibenzoylmethane complex, sustaining a bathochromic shift on adduct formation.

## Magnetic susceptibility measurements

The moment usually observed for magnetically dilute Cu (II) complexes is between 1.7-2.2 BM with compounds whose geometry approaches octahedral geometry having moments at the lower end while those approaching tetrahedral geometry are at the higher end (Hugee et al., 1993).

The magnetic moment value of [Cu(dbm)$_2$(H$_2$O)$_2$] complex is 1.80 B.M which suggests a distorted octahedral geometry around the metal ion.

## Kinetics of the reaction

Plots of $-\ln(A_\alpha-A_t)$ versus time resulted in straight line graphs. The slopes of the graphs were the observed pseudo first order rate constant, k$_{obs}$. Table 3 reports the k$_{obs}$ values against the various concentrations of the ligand (dbm).

For each metal concentration, a graph of kobs values against the various concentrations of the ligand serves as a basis for suggesting the rate law that governs the reaction between Cu (II) and dbm. The nature of the profiles shown in Figure 1 (a to d) suggests a rapid pre-equilibrium mechanism (Odiaka, 2004) involving the formation of an intermediate prior to the formation of the product. The intermediate is formed instantaneously followed by a slow rate determining step (k$_2$) leading to the formation of the product. The proposed mechanism for the reaction of Cu (II) and dbm methane is shown as follows:

$$Cu^{2+} + DBM \longrightarrow Int \longrightarrow product(p). \qquad (1)$$
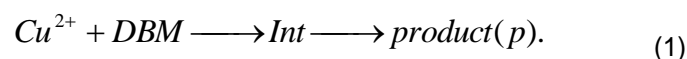
Since the rate of reaction is governed by the slow step, then the rate for Equation (1) is given by

$$\text{Rate} = \frac{dp}{dt} = k_2 \left[DBM\right]\left[Int\right] \qquad (2)$$

The pre – equilibrium constant for intermediate formation is given by Equation (3)

$$k_1 = \frac{\left[Int\right]}{\left[Cu^{2+}\right]\left[DBM\right]} \qquad (3)$$

The [Int] is given by

$$[Int] = k_1 \left[Cu^{2+}\right] \left[DBM\right] \qquad (4)$$
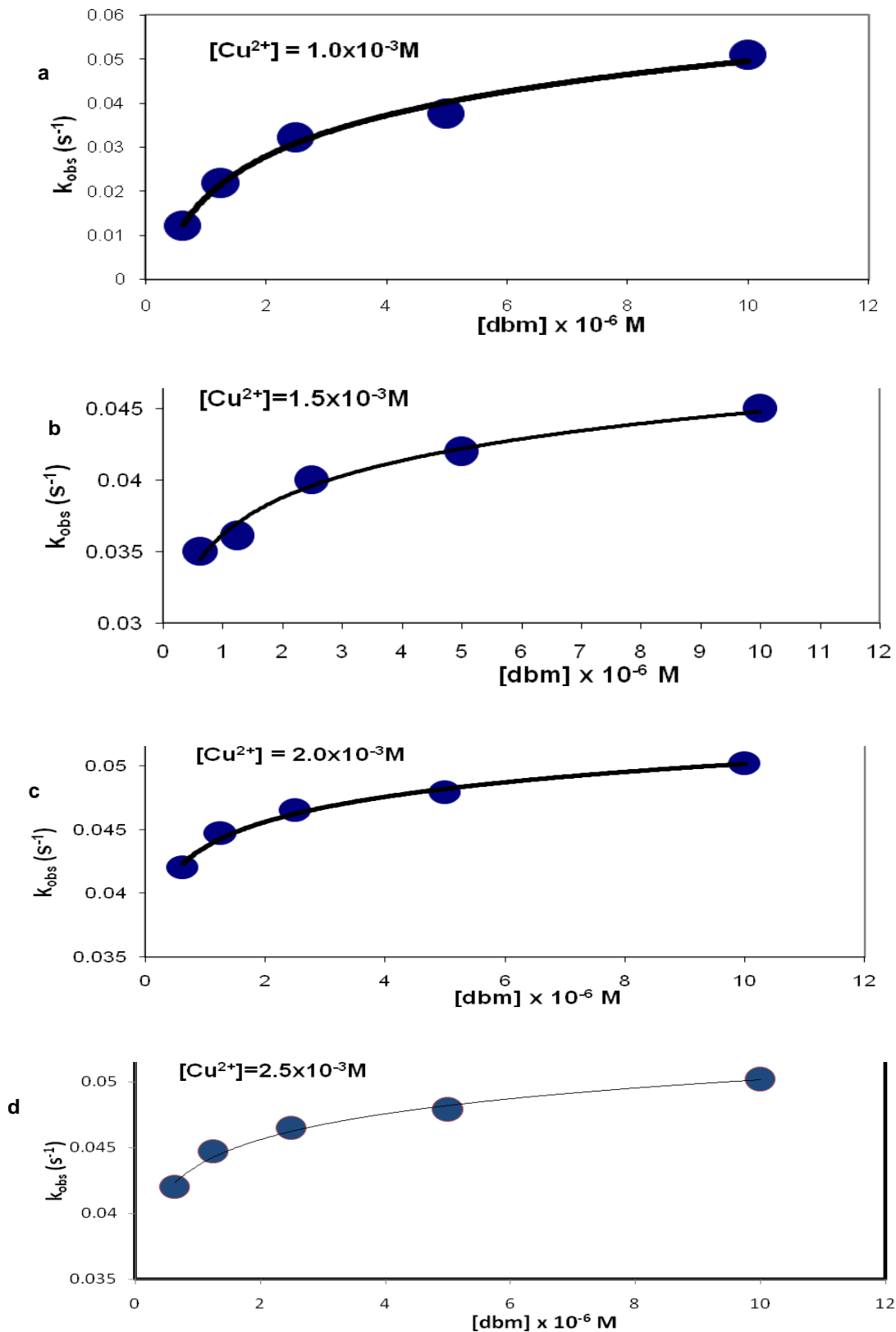
Substituting (4) into (2)

**Figure 1.** a. The plot of pseudo first order rate constant, ($k_{obs}$) against the concentration of dbm, [dbm] at 298 K for $Cu^{2+}$ = 1.0 x$10^{-3}$M; b. The plot of pseudo first order rate constant, ($k_{obs}$) against the concentration of dbm, [dbm] at 298 K for $Cu^{2+}$ = 1.5 x$10^{-3}$M; c. The plot of pseudo first order rate constant, ($k_{obs}$) against the concentration of dbm, [dbm] at 298 K for $Cu^{2+}$ = 2.0 x$10^{-3}$M; d. The plot of pseudo first order rate constant, ($k_{obs}$) against the concentration of dbm, [dbm] at 298 K for $Cu^{2+}$ = 2.5 x$10^{-3}$M.

**Table 4.** Rate constants for the formation of intermediate and product.

| [$Cu^{2+}$] x $10^{-3}$ M | $k_1$ x $10^5$($s^{-1}$) | $k_2$($s^{-1}$) (T) | $k_2$($s^{-1}$) (I) |
|---|---|---|---|
| 1.0 | 0.49 ±0.02 | 0.051±0.03 | 0.052±0.02 |
| 1.5 | 3.7±0.01 | 0.045±0.01 | 0.043±0.03 |
| 2.0 | 10.0±0.03 | 0.050±0.02 | 0.049±0.01 |
| 2.5 | 17.2±0.02 | 0.058±0.01 | 0.058±0.02 |

T= Tangent of $k_{obs}$ vs [DBM] graphs; I= Inverse of the intercept of $\dfrac{1}{k_{obs}}$ vs $\dfrac{1}{[DBM]}$ graphs.

$$\text{Rate} = \frac{dp}{dt} = k_2\, k_1\, [Cu^{2+}][DBM]^2 \qquad (5)$$

Experimentally, we followed the disappearance of the [Int] and [$Cu^{2+}$]. Hence

$$\text{Rate} = \frac{dp}{dt} = k_{obs}\left\{[Cu^{2+}]+[Int]\right\} \qquad (6)$$

$$\text{Rate} = \frac{dp}{dt} = k_{obs}\left\{[Cu^{2+}]+k_1[Cu^{2+}][DBM]\right\} \qquad (7)$$

Substituting (4) into (6) we have

$$\text{Rate} = \frac{dp}{dt} = k_{obs}\ [Cu^{2+}]]\left\{1+k_1[DBM]\right\} \qquad (8)$$

From Equation (5 and 8). Rate = $k_2\, k_1$ [$Cu^{2+}$] [DBM]$^2$

$$= k_{obs}\,[Cu^{2+}]\left\{1+k_1[DBM]\right\} \qquad (9)$$

$$\therefore k_{obs} = \frac{k_2\, k_1\,[DBM]^2}{1+k_1[DBM]} \qquad (10)$$

Equation (10) is the general rate expression for a pre-equilibrium mechanism. The intermediate in Equation (1) was not attacked by a nucleoplile that is DBM. It only rearranges in a rate determining manner to form the product.
Then Equation 10 reduces to Equation (11)

$$\therefore k_{obs} = \frac{k_2\, k_1\,[DBM]}{1+K_I\,[DBM]} \qquad (11)$$

The intermediate in Equation (1) was formed rapidly.

Then $k_1$ in Equation (11) must be very large such that $k_1$ [DBM] is so large that we can reasonably ignore 1 in

Equation 11 which now collapses to Equation (12)

$$k_{obs} = k_2 - \qquad (12)$$

Equation (12) explains the extrapolation of the flattened portion of the graph to the $k_{obs}$ axis which results in getting $k_2$ (tabulated in Table 4). Inversion of equation 11 yields.

$$\frac{1}{k_{obs}} = \frac{1}{k_2 k_1 [DBM]} + \frac{1}{k_2} \qquad (13)$$

Therefore plots of $\dfrac{1}{k_{obs}}$ versus $\dfrac{1}{[DBM]}$ results in straight lines (Figure 2 a to d) whose slope = $\dfrac{1}{k_2 k_1}$

From where $k_1$ values are obtained and intercept on the y-axis = $\dfrac{1}{k_2}$

**Conclusion**

The reaction between Cu (II) and dbm follows a rapid pre-equilibrium mechanism. Although, the rate of complex formation ($k_2$) is constant for various metal concentration (Table 4) and is independent of the metal concentration. This suggests an interchange associative ($I_a$) mechanism, implying that bond making is important than bond breaking.
   The $k_1$ value obtained is lower than the expected value for water exchange rate ($10^5 \leq 10^8$ $M^{-1}s^{-1}$) hence, it is suspected that the formation of the intermediate is not strictly the loss of water from the Cu(II) ions, but some metal – ligand bond formation takes place before the Cu-$OH_2$ bond is completely broken.
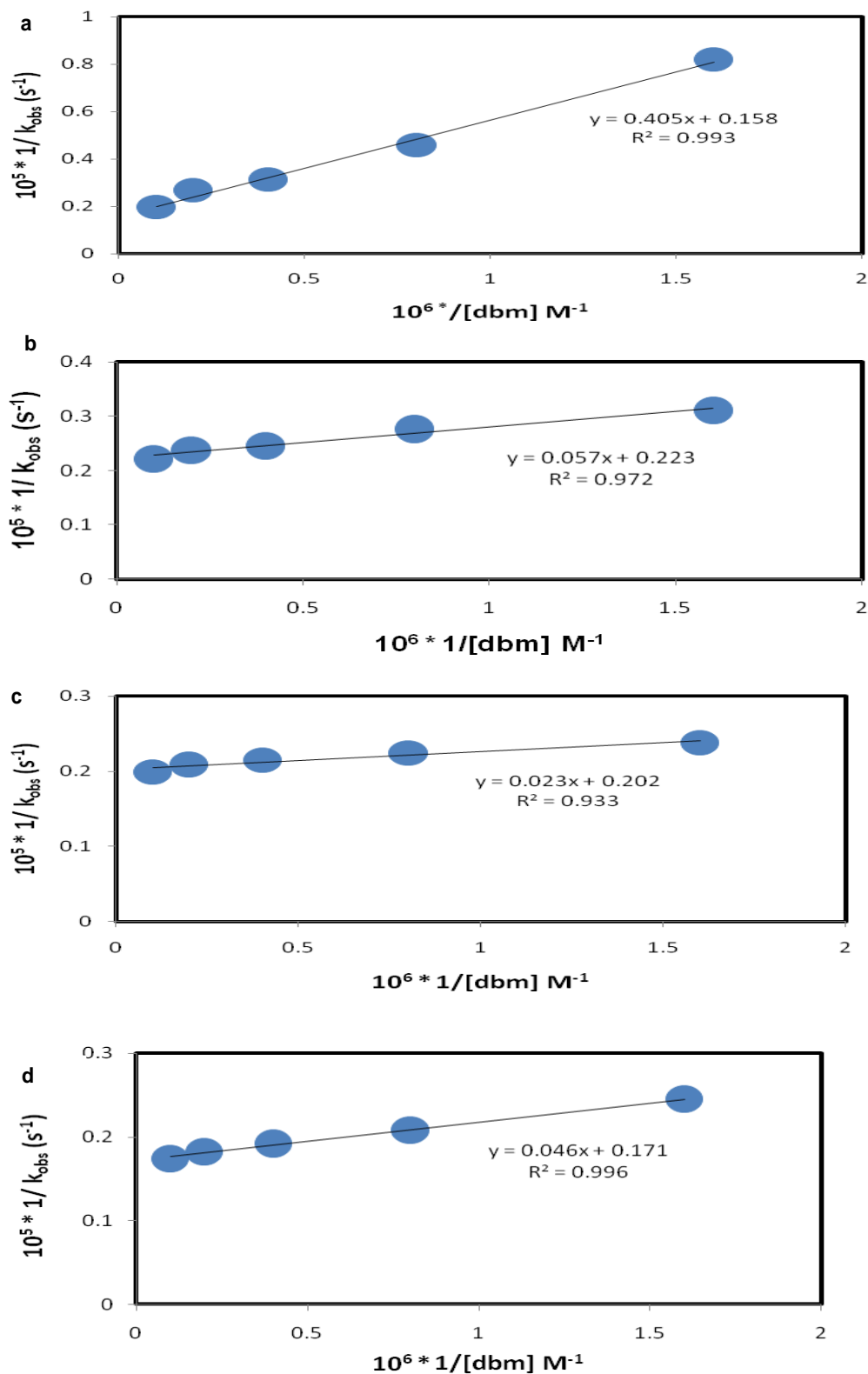
**Figure 2 a.** Plot of inverse of pseudo first order rate constant, $(1/k_{obs})$ against inverse of $[dbm]$, $(1/[dbm])$ at 298K for $[Cu^{2+}] = 1x\ 10^{-3}$ M; b. Plot of inverse of pseudo first order rate constant, $(1/k_{obs})$ against inverse of $[dbm]$, $(1/[dbm])$ at 298K for $[Cu^{2+}] = 1.5x\ 10^{-3}$ M; c. Plot of inverse of pseudo first order rate constant, $(1/k_{obs})$ against inverse of $[dbm]$, $(1/[dbm])$ at 298K for $[Cu^{2+}] = 2.0x\ 10^{-3}$ M; d. Plot of inverse of pseudo first order rate constant, $(1/k_{obs})$ against inverse of $[dbm]$, $(1/[dbm])$ at 298 K for $[Cu^{2+}] = 2.5 \times 10^{-3}$ M.

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