J. Mater. Environ. Sci. 3 (6) (2012) 1101-1108 *El-Shafaia et al.*
ISSN : 2028-2508
CODEN: JMESCN

Synthesis and Characterization of tris(hydroxybenzylaminoethyl)amine-based Zinc(II), Copper(II), and Cobalt(II) Complexes-containing Bound Benzenethiol: Their Applications Toward Methylation Reactions

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Received 18 June 2012, Revised 20 July2012, Accepted 20 July 2012
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Abstract

Three transition metal-bound thiolate complexes $[LZn-SC_6H_5]^+$ **1**, $[LCu-SC_6H_5]^+$ **2**, and $[LCo-SC_6H_5]^+$ **3**, derived from the tetradentate ligand *N,N',N''*-tris(*p*-hydroxybenzylaminoethyl)amine, L were synthesized and characterized as functional models for the active site of thiolate alkylating enzyme. Solid state studies of these model complexes were investigated using infrared spectroscopy and both thermal and elemental analyses. The methylation reactions of these thiolate complexes were found to be the fastest at high concentrations of CH_3I in the sequence of **3** > **2** > **1**. These obtained results showed that there are significant increases in the rate of methylation of the thiolate complexes with cobalt(II) metal ion than other metal ions, due to its high electrophilicity. Where it can activate the thiolate nucleophile most effectively than other metal ions. Zinc(II) is the opposite and has the lowest methylation reactions.

Keywords: Transition metal complexes; Tetradentate ligand; Thiolate; Alkylation

Introduction

Many efforts have been made for investigating the alkylation reactions by using a series of zinc(II) complexes containing bound thiolate. Wilker and Lippard showed that in the reaction of $[Zn(SPh)_4]^{2-}$ with trimethylphosphate, the attacking nucleophile was attributed to the free thiolate anion, which derived from the parent thiolate complex [1,2]. Parkin [3,4] and Vahrenkamp [5-10] have alkylated the zinc(II)-bound thiolate complexes $Tm^{Ph}ZnSR$ and TpZnSR (Tm = tris(thioimidazilyl)borate and Tp = tris(pyrazolyl)borate) with CH_3I to investigate the reactivity of the zinc thiolate linkage in a sulfur rich environment [1-10]. Carrano [11-15] has studied the question whether the thioethers resulting from zinc-thiolate alkylation are still coordinated to zinc. Very recently, we have [16-24] also showed that the resulting thioethers from the methyltaion of zinc-bound thiolate are still coordinated to the zinc centre.

The diamagnetic d^{10} zinc(II) center of the native enzyme offers little in terms of a spectroscopic probes. For this reason, the investigation of metal-substituted enzymes (e.g., Co, Ni, and Cu) has been actively pursued in order to provide information concerned with both enzyme structure and activity [25-28]. Central to such research is the existence of a series of both structurally and spectroscopically well-characterized model complexes that thereby allow comparisons to be made with the metal-substituted enzymes.

The purpose of the present work was (i) designing and synthesizing different forms of mononuclear metal (Zn^{2+}, Cu^{2+}, and Co^{2+}) thiolate complexes containing N_4S environment as structural models for the active site of thiolate alkylating enzymes and (ii) studying their methylation reactions with methyl iodide as an alkylating agent. Toward these aims, *N,N',N''*-tris(*p*-hydroxybenzylaminoethyl)amine L as a tetradentate ligand was used for the synthesis of three transition metal thiolate complexes (Scheme 1). Benzenethiol was selected as thiolate coligand for the syntheses of these model complexes. The kinetic studies of these thiolate complexes toward methylation reaction using methyl iodide as an alkylating agent have been studied using UV-visible spectroscopy.

Experimental

2.1. General

All reagents and solvents used were of analytical grade. Zinc perchlorate hexahydrate, copper(II) bromide, and cobalt(II) bromide, were Purchased from Aldrich. P-hydroxobenzaldhyde and benzenethiol were purchased from CALOERB Division Chemical, tris(2-aminoethyl)amine, and methyl iodide were obtained from Aldrich. The hydrogen, carbon, and nitrogen contents of the ligands and their metal complexes were measured by micro analytical procedure using Elementary III CHNS Analyzer Germany. The IR absorption spectra of the ligands and their coordination compounds were recorded using FT-IR Bruker Vector22 Spectrometer, Germany in the range of 400-4000 cm^{-1}. The ^{1}H NMR measurements were recorded in deutrated dimethyl sulfoxide (DMSO-d$_6$) at 303.1 K by using Mercury-300 BB 'NMR300' and Gemini-200 'NMR'.

2.2. Syntheses

2.2.1. Tris(p-hydroxybenzylaminoethyl)amine trihydrobromide (L •3HBr)

Tris(2-aminoethyl)amine (0.51 mL, 3.4 mmol) and *p*-hydroxobenzaldhyde (1.25 mg, 10.26 mmol) were dissolved in methanol (20 mL) and vigorously stirred at room temperature , and refluxed for 2h. A yellow precipitate was formed on cooling, filtered off ,washed out with methanol ,and dried in *vacuo*. The obtained tris-imine (12.6 mmol) was reduced by a solution of $NaBH_4$ (40 mmol) in methanol and the reaction was let to stir overnight. The resultant solution was acidified by concentrated solution of HBr. A pale gray precipitate of rhe ligand tris(*p*-hydroxobenzylaminoethyl)amine trihydrobromide (L· 3HBr) was formed, filtered, washed out with diethyl ether, and dried up. m. p. > 300 (decomp.). Yield = 57.8 mg (79.4 %). ^{1}H NMR (DMSO-d$_6$): δ = 2.81 [m, 6H, CH_2^{α}], 3.09 [m, 6H, CH_2^{β}], 4.08 [s, 6H, CH_2^{γ}], 6.77 - 6.81 [d, 6H, $CH_{Ph}(2,6)$], 7.32 - 7.36 [d, 6H, $CH_{Ph}(3,5)$], and 8.73 ppm (br, 3H, NH). FT-IR (KBr): ν (cm^{-1}) = 3380 (s, O-H), 3255 (s, N-H), 2958-2796 (s, C-H$_{aromatic}$), and 1607 cm^{-1} (s, C=C).

*2.2.2. {tris(p-hydroxybenzylaminoethyl)aminethiophenolatozinc}perchlorate **1***

99 mg (0.014 mmol) of the ligand L in methanol was added to a stoichiometric amount of $Zn(ClO_4)_2{\cdot}6H_2O$ (52 mg, 0.0142 mmol) in methanol. The mixed solution was stirred for around 3h., then add a solution of C_6H_5SNa, which made up from (29 ml, 0.028 mmol) of thiophenol and (15 mg, 0.028 mmol) of CH_3ONa in (10 ml) of methanol, the addition was dropwise and very slowly, the reaction was let to stir overnight at room temperature, filtered off, washed out with diethyl ether, and dried up. m. p >300 (decompose). Yield = 68.5 mg (61.11 %). ^{1}H NMR (DMSO-d$_6$): δ = 2.71 [m, 6H, CH_2^{α}], 3.00 [m, 6H, CH_2^{β}], 4.01 [s, 6H, CH_2^{γ}], 6.69 - 6.78 [d, 6H, $CH_{Ph}(2,6)$], 7.18 - 7.22 [d, 6H, $CH_{Ph}(3,5)$], and 9.83 (br, 3H, NH), and 10.40 ppm (m, 3H, OH). FT-IR (KBr): ν (cm^{-1}) = 3415 (s, O-H, N-H), 3060 (m, C-H$_{aromatic}$), 2959 (m, C-H$_{aliph}$), 1615 (m, C=C), and 1100 cm^{-} (ClO_4^-).

*2.2.3. {tris(p-hydroxybenzylaminoethyl)aminethiophenolatocopper}bromide **2***

113 mg (0.016 mmol) of the ligand L in methanol was added to a stoichiometric amount of $CuBr_2$ (35 mg, 0.016 mmol) in methanol. The mixed solution was stirred for around 3h., then add a solution of C_6H_5SNa, which made up from (0.033 ml, 0.031 mmol) of thiophenol and 17 mg (0.031 mmol) of CH_3ONa in 10 ml of methanol, the addition was dropwise and very slowly, the resulting solution was let to stir overnight at room temperature, filtered off ,washed out with diethyl ether, and dried in *vacuuo*. m. p. >300 (decomp.). Yield = 70.31 %. (84.3 mg). FT-IR (KBr): ν (cm^{-1}) = 3414 (s, O-H, N-H), 2926 (m, C-H$_{aromatic}$), and 1615 cm^{-1} (m, C=C).

*2.2.4. {tris(p-hydroxybenzylaminoethyl)aminethiophenolatocobalt}bromide **3***

111 mg (0.016 mmol) of the ligand L in methanol was added to a stoichiometric amount of $CoBr_2{\cdot}H_2O$ (37.14 mg, 0.16 mmol) in methanol. The mixed solution was stirred for around 3h., then add a solution of $NaSC_6H_5$, which made up from benzenethiol (0.032 ml, 0.31 mmol) $NaOCH_3$ (16.9 mg, 0.31 mmol) in 10mL of methanol, the addition was dropwise and very slowly , the reaction was let to stir overnight at r. t., filtered off , washed out with diethyl ether, and dried. m. p > 300 °C (decomp.). Yield = 65.26 %.(78.5 mg). FT-IR (KBr): ν (cm^{-1}) = 3420 (b, O-H, NH), 2931 (w, C-H$_{aromatic}$), and 1675 cm^{-1} (m, C=C).

2.3. Thermal analysis

The non-isothermal kinetic measurements for the decomposition of these metal(II)-bound thiolate complexes were carried out by the application of Coats-Redfern [29]. The kinetic parameters (*E* and *n*) were calculated according to the above method and their values are tabulated under the thermogram of each complex. The activation enthalpy (ΔH^*), the activation entropy (ΔS^*), and the free energy of activation (ΔG^*) were calculated using the following equations: $\Delta H^* = E - RT$, $\Delta S^* = R[ln(Ah/kT)-1]$, and $\Delta G^* = \Delta H^* - T\Delta S^*$. Where *A*, *K*, and *h* are the pre-exponential factors, Boltzman, and plank constants, respectively [30].

2.3. Kinetik measurements for the reaction of thiolate complexes with methyl iodide

All experiments were performed under pseudo-first-order conditions with the large excess of methyl iodide. In a typical experiment, 10 mM of the thiolate complex was dissolved in (methanol or ethanol) followed by addition of 3-9 equivalents of methyl iodide. All the reactions were monitored by UV-visible spectroscopy at 300 K. The UV-visible absorption bands of the produced methyl phenyl thioether (CH_3-S-C_6H_5) were used as standard. The increase in the absorbance of the produced compounds was recorded. The UV-visible measurements were done at intervals of times. The first order rate constants were calculated from the slopes of the linear plots of ln (1-A_t/A_o) versus time. The second order rate constants were calculated from the knowing the 1st order rate constants at different concentrations.

3. Results and Discussions

3.1. Synthesis of the ligand L and its thiolate model complexes

In order to model the structure and function in the active site of metal-containing enzyme, a new ligand L has been synthesized. It has a big hydrophobic cavity hoped to enhance the stability of the metal complexes, which at the same time may favor the activation of the substrate during the catalytic reactions.

Based on the success of the tris(benzylaminoethyl)amine, as a ligand for metalloenzyme modelling studies [33]. We have modified it and synthesized a new water soluble tripod ligand namely, N, N, N-tris(*p*-hydroxybenzylaminoethyl)amine L by the condensation reaction between tris(2-aminoethylamine) and three equivalent amounts of *p*-hydroxybenzaldehyde in absolute methanol (Scheme 1). The produced imine was reduced by using sodium tetrahydro-borate in methanol, which was precipitated in the acidified form using hydrobromic acid. The ligand L was crystallized from methanol (95 %) and obtained analytically pure with high yield. The ^{1}H NMR spectrum of the ligand L showed the disappearance of the aldehyde singlet and appearance of a new imine signal at 8.61 ppm. It exhibited also clearly resolved resonances for the methylene hydrogens. Most characteristics are the IR spectra (Figure 2), which showed ν(O–H), ν(N–H), and ν(C–H) absorption bands at around 3380 (br), 3255 (br), and 2958-2796 (s) cm$^{-1,}$ respectively for both the ligand and its complexes.

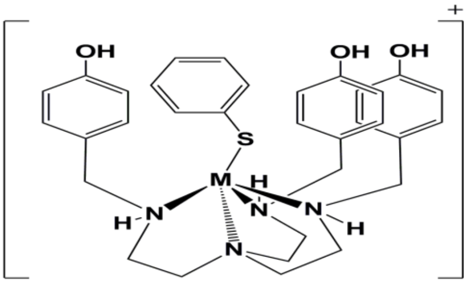
The ligand L was used to emulate the coordination environment provided by the histidine protein residues in metalloenzymes. Herein we extend the coordination chemistry of this ligand system with the synthesis of simple metal thiolate complexes $[LM\text{-}SR]^+$ with three different metal ions ((Zn^{2+}, Cu^{2+}, and Co^{2+}) and benzenethiol as a coloigand. These model complexes were characterized using FT-IR, UV-visible, and ^{1}H NMR spectroscopes as well as conductometric titrations and thermal analyses.

To determine the effect of the nature of the coordinated metal atoms in the coordination sphere of L upon sulfur nucleophilicity and the rate of thiolate methylation. We describe herein the synthesis of a series of LM(II) thiolate complexes **1-3** with benzenethiol as a coligand and different transition metal ions.

The monomeric LZn-bound thiophenolate complex, [LZn-SC_6H_5]ClO_4 **1**, was obtained by treating the *in situe* formed perchlorate [LZn(H_2O)](ClO_4)$_2$ complex [31] with equivalent amount of the deprotonated form of benzenethiol in absolute methanol at room temperature. The zinc(II) complex 1 was precipitated from the reaction solution as white powder. The ^{1}H NMR spectra in DMSO-d_6 show the aliphatic methylene protons as well as the aromatic CH protons of the *p*-hydroxophenyl groups are shifted to downfield compared to those of the free ligand. The IR spectrum of complex 1 showed strong absorption band at 1100 cm^{-1}, which is assigned as ν(ClO) bands of the perchlorate anions. This shift is in the range of different complexes containing the same perchlorate anion [32], in which the presence of hydrogen bonds was evidenced.

Treating of the in *situ* formed [L-Zn-OH_2](ClO_4)$_2$, [L-Cu-Br]Br, and [L-Co-Br]Br with equivalent amounts of benzenethiol under the same conditions yielded their thiolates analogues [L-Zn-SC_6H_5] **1**, [LCu-SC_6H_5]Br **2**, and [LCo-SC_6H_5]Br **3**, respectively. The isolated complexes were analytically pure with high yields. The colour of the complex **1** was colourless, whereas of **2** and **3** were colored. These prepared thiolate complexes were stable at room temperature. The elemental analysis (C, H, and N) showed that the experimental and calculated values are in good agreements with the proposed structure. The IR spectra are almost similar for both complexes. The phenolic ν(OH) and imine ν(NH) absorption bands in complexes **1-3** are overlapped with each other and they are shifted to higher frequencies compared to those found in the ligand itself. This may indicate that the ligand is coordinated to the metal ions through the imine nitrogens as well as the tertiary nitrogens. Attempts to propose the structure of the isolated thiolate complexes come from their investigation using thermal analysis studies.

Scheme 1: The structure of the metal(II) complexes 1-3



[LM-SC₆H₅]⁺

Complex	**1**	**2**	**3**
M	**Zn**	**Cu**	**Co**

Thermal studies of the model complexes

The thermal decomposition of the zinc(II) complex **1** was recorded at temperature range of 25 - 900 ^{o}C. The TGA-DTG curve of complex 1 (Figure 1) exhibits several thermal events. The first step in the TG plot corresponds to the explosion of three molecules of water of crystallization (Calc. 7.7 %, Found 7.6 %) have activation energy of 23.6 kjmol^{-1} and first order reaction. The second step due to the elimination of the perchlorate counter anion $(ClO_4)^-$ Calc. 10 %, Found 9.6 %). The following steps were not suitable for precise investigations. The final stable residue as idenetified from the mass loss consideration is Zn (Calc. 8.27 %, Found 8.20 %).

Table 1. Physical and analytical data of the ligand L and their omplexes **1-3**

Compound	Found(Calc.%)				
	%C	%H	%N	%Cl	%M
$C_{27}H_{36}N_4O_3 \cdot 3HBr$ L	45.02(45.48)	4.98(5.52)	8.37(7.92)	---	---
$[L\text{-}Zn\text{-}SC_6H_5](ClO_4)\cdot 3H_2O$ $C_{33}ClH_{47}N_4O_{10}SZn$ (**1**)	50.33(50.00)	5.78(5.98)	7.15(7.07)	4.23(4.47)	8.34(8.25)
$[L\text{-}Cu\text{-}SC_6H_5]Br\cdot CH_3OH\cdot 3H_2O$ $C_{34}H_{51}N_4O_7BrCu$ (**2**)	53.13(52.95)	6.77(6.67)	7.12(7.26)	---	8.32(8.24)
$[L\text{-}Co\text{-}SC_6H_5]Br\cdot 3H_2O$ $C_{33}H_{47}N_4O_6BrCo$ (**3**)	52.99(53.96)	6.42(6.45)	7.76(7.63)	---	7.98(8.02)

The copper(II) thiolate complex **2** slowly started to decompose at 27 ^{o}C (**Figure 1**). The first mass loss (Calc. 7.0 %, Found 6.9 %) up to 112 ^{o}C is in a good agreement with the loss of three water molecules, which has a DTG peak at 60 ^{o}C. This is immediately followed by decomposition process in the range of 112 - 205 ^{o}C with mass loss of (Calc. 14.5 %, Found 14.9 %), due to the pyrolysis of one methanol molecule and one bromine atom. The third stage take place between 206 and 850 ^{o}C and is accompanied by mass loss of (Calc. 74.3 %, Found 74.0 %). It is attributed to the decomposition of the remained organic part. The final stable residue as identified from the mass loss consideration is Cu (Calc. 8.2 %, Found 7.8 %).

The TG plot of the cobalt(II) thiolate complex **3** (**Figure 1**) showed that it was decomposed in five main successive overlapped steps. The first decomposition step occurred in the temper-ature range 27 - 140 ^{o}C with a net weight loss of (Calc. 17.4%, Found 17.0 %). This is consistent with the decom-position and elimination of three water molecules and one bromine atom. The second, third, and fourt stages occurred in the range of 140 - 850 ^{o}C with a total weight loss of (Calc. 74.7 %, Found 74.4 %). This is corresponding to the decomposition of the remaining organic part. The metallic cobalt residue was left as a final decomposition product with a percentage weight loss of (Calc. 7.7 %, Found 8.0%).

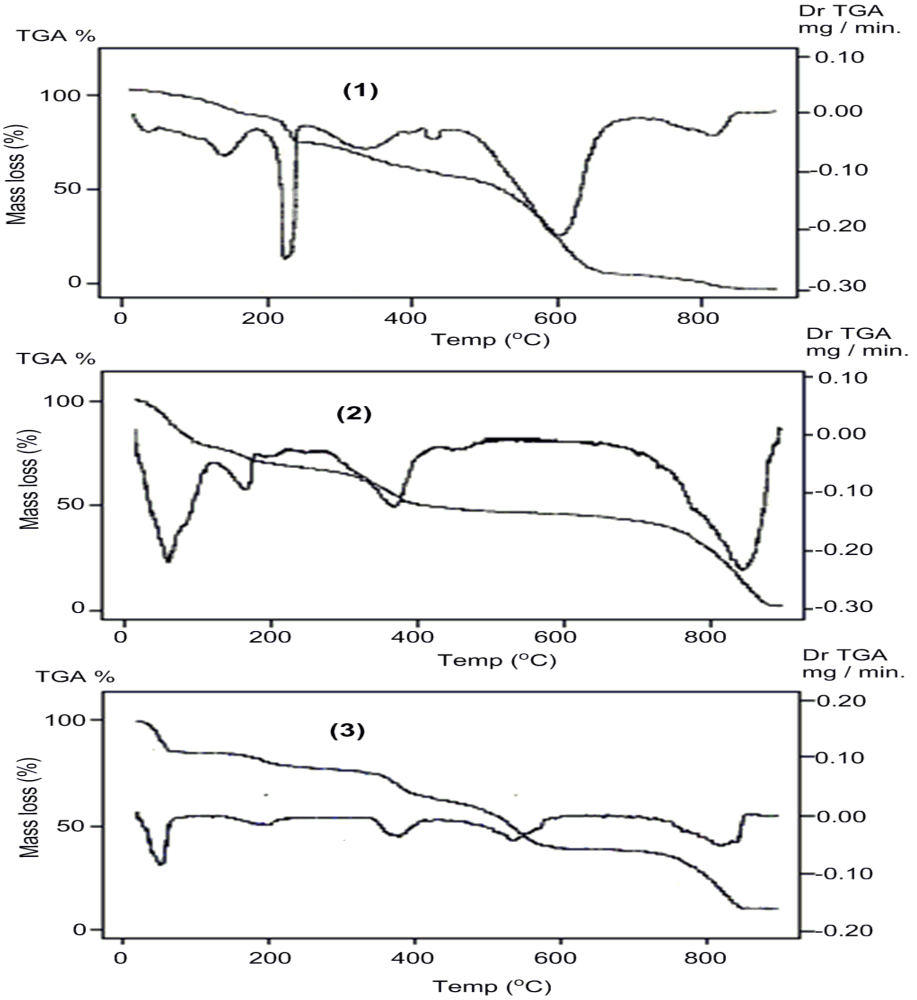


Figure 1 : TGA-DTG curves of metal(II) complexes 1-3

The kinetic parameters ($\Delta E^{\#}$) and the thermodynamic parameters ($\Delta S^{\#}$),($\Delta H^{\#}$) and ($\Delta G^{\#}$) also have been calculated for every step for complex decomposition (Table 2). The low values of ΔE for the first and second steps in the zinc(II)-bound thiophenolate complex **1** indicate that the water molecules as well as the perchlorate anions are not coordinated to the zinc metal. Whereas, the relatively high values for the decomposition steps of the organic part of the cation $[LZn\text{-}SC_6H_5]^+$ indicate that the ligand tris(p-hydroxy-benzylaminoethyl)amine and the coligand thiophenolate are strongly coordinated to the zinc(II) ion. The negative values of ΔS^* in the second and third steps indicate that the activated complex have more ordered structure than the reactants and the reactants are slower than the metal [33]. The low high values of the activation energies *E* for the first and second decomposition steps in the copper(II)-bound thiophenolate complex **2** as well as the organic part in comparison to that of complex **1** indicates the high stability of copper complex. The negative values of ΔS^* in the second and third steps indicate that the activated complex have more ordered structure than the reactants and the reactants are slower than the metal.

4. Kinetic investigation for the methylation reactions

Reactions of the metal(II)-bound thiolate complexes **1-3** with methyl iodide in methanol results in the quantitative formation of ethylthioethers and LM(II)-bound iodide complexes as indicated in scheme 2.

Table 2. Kinetic and thermodynamic data of complexes **1 - 3**.

Complex	step	ΔG (kJmol^{-1})	ΔS (Jk^{-1}mol^{-1})	ΔH (Jmol^{-1})	ΔE (Jkmol^{-1})	ΔG (kJmol^{-1})	R
$[LZn\text{-}SC_6H_5]^+$ (**1**)	1 St	373	23.56	20.65	-0.221	103.26	0.996
	2 nd	489	16.57	13.65	-0.232	127.00	127.00
	3 rd	573	55.83	52.92	-0.194	164.13	164.13
	4 th	715	113.98	111.06	-0.121	197.36	197.36
	5th	940	91.62	88.70	-0.206	282.50	282.50
	6th	1140	297.78	294.86	-0.037	336.89	336.89
$[LCu\text{-}SC_6H_5]^+$ (**2**)	1 St	315	54.53	51.61	-0.104	84.46	84.46
	2 nd	378	52.19	49.27	-0.138	100.73	100.73
	3 rd	486	51.72	48.79	-0.183	137.42	137.42
	4 th	731	32.66	29.74	-0.241	205.76	205.76
	5th	1298	123.34	120.42	-0.218	402.70	402.70
$[LCo\text{-}SC_6H_5]^+$ (**3**)	1 St	323	85.91	82.99	-0.008	85.58	85.58
	2 nd	556	32.63	29.71	-0.236	161.00	161.00
	3 rd	723	82.11	79.19	-0.181	209.98	209.98
	4 th	864	025.47	122.55	-0.154	255.67	255.67
	5 th	1148	166.20	163.28	-0.163	349.89	349.89

The measurements were performed at 300 K. The rates of reaction were monitored by UV-visible spectral changes which exhibited increase and decrease in the intensities of the iodo metal complex and metal(II)-bound thiolate complex, respectively. Under pseudo-first-order conditions, the methylation exhibited first-order kinetics over at least five half lives. The reactions obeyed second-order rate law. i.e, first order in each reagent. The pseudo-first-order constants k_{obs} were obtained according to equations 1-5 and the 2nd order rate constants were calculated:

$$-d[CH_3I] / dt = k_{obs} [CH_3I] \qquad (1)$$

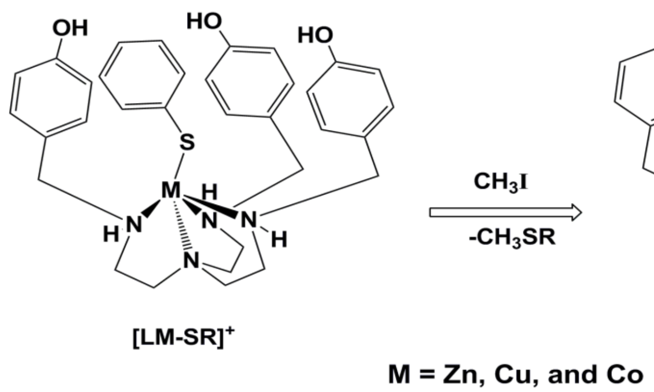
$$\ln[C_t] / [C_o] = -k_{obs}\, t \qquad (2)$$

$$\ln\{[C_{inf}(CH_3SR) - C_t(CH_3SR)] / C_{inf}(CH_3SR)\} = -k_{obs}\, t \qquad (3)$$

$$\ln\{[A_\infty(CH_3SR) - A_t(CH_3SR)] / A_\infty(CH_3SR)\} = -k_{obs} \qquad (4)$$

$$k_{obs} = k\, [CH_3I] \qquad (5)$$

To determine the effect of the nature of the bound metal ions upon the rate of thiolate methylation. The kinetic reactions of thiolate complexes **1-3** with methyl iodide were comparatively investigated. The methylation reactions were followed in UV-visible at 300 K by monitoring the increase in the absorbance of the phenyl ring of the produced methyl l phenyl thioether, CH_3SAr at λ_{max} = 250 nm. A typical UV-visible spectra and representative time courses for the methylation reaction as a function of time is shown in **Figure 2** for the copper(II)-bound thiolate complex. The reactions of the metal(II)-bound thiophenolate complexes **1-3** with CH_3I were fastest at high concentrations of CH_3I in the sequence of **3** > **2** > **1** and the pseudo-first order rate constants at different concentrations of CH_3I were calculated and showed in **Table 3**. The values of the second order rate constant, k_2 were estimated to be 0.0347, 0.069, and 0.153 $M^{-1}S^{-1}$ for the model complexes **1-3**, respectively. These obtained results showed that there are significant increases in the rate of methylation of the thiolate complexes: with copper(II) metal ion than other metal ions, where its most effective electron-withdrawing ion and has the greatest electrophilicity. There it can activate the thiolate nucleophile most effectively than other metal ions. Zinc(II) is the opposite and has the lowest methylation reactions.



Scheme 2: The kinetic reaction of the metal(II) complexes with methyl iodide

Table 3. Pseudo first order rate constants for the methylation of the thiolate complexes 1-3 at different concentrations of MeI in methanol at 25 °C.

Complex	MeI [x 10^{-3}M]	k_{obs}, s^{-1}
(**1**)	0.95	0.061
	1.43	0.088
	1.90	0.094
	2.38	0.114
	2.86	0.320
(**2**)	2.86	0.106
	4.29	0.217
	5.73	0.263
	7.16	0.402
	8.58	0.412
(**3**)	2.66	0.136
	4.29	0.576
	5.72	0.758
	7.16	0.990
	8.58	1.026

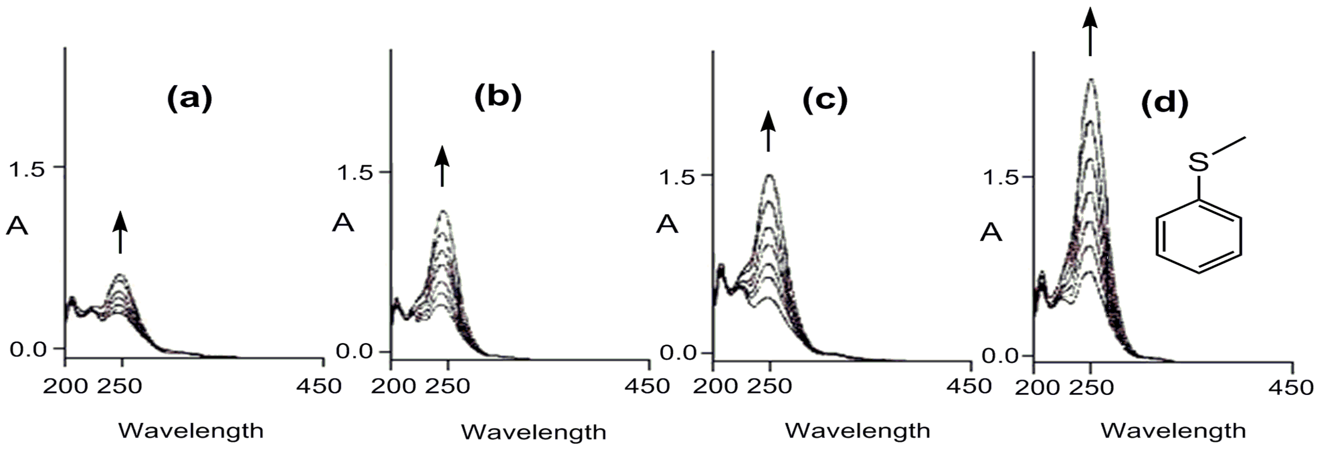


Figure 2: Uv-visible spectra and thier semilogarythmic plots for the methylation reactions of $[L\text{-}Cu\text{-}SC_6H_5]^+$ 2 (1.0375x 10^{-5} M), by using methyl iodide at different concentrations : (a) 2.862 x 10^{-3} M, (b) 4.293 x 10^{-3} M , (C) 5.724 x 10^{-3} M, and (d) 7.155 x 10^{-3}M

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(2012) ; http://www.jmaterenvironsci.com