The Eurasia Proceedings of Science, Technology,
Engineering & Mathematics (EPSTEM)
ISSN: 2602-3199

The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 2019

Volume 7, Pages 220-227

IConTES 2019: International Conference on Technology, Engineering and Science

Characterization and Comparison of the Reaction Product of (Pd, Pt, Ag and Au) in Different Solvent with Diaminothiuramdisulfide

Afyaa M.YOUNUS
University of Mosul

Ihsan A. MUSTAFA
University of Mosul

Abstract: The work presented in research describes the preparation and characterization of new complexes resulted from the reaction of diaminothiuramdisulfide(tds)with metals (or metals chlorides)of group(VIII)[Na2pdcl4,Pt(0) and K2ptcl4]in addition to group(IB)metals[Ag(0) ,AgCl and Au(o)]. The thiuramdisulfide compound (tds) reduced to the corresponding aminodithiocarbamate anion (H2NNHCS2)-in some complexes(Oxidative addition reaction) However, in the remaining complexes the (tds)were simply added to the metal chloride (addition reaction) without cleavage of the –S-S-bond.the resulting complexes can be classified as follows.

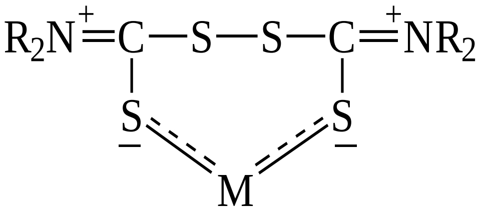
I-The oxidative addition reactions offered complexes of the type:
1-[M(L)2]((Where L=H2NNHCS2-(aminodithiocarbamate anion) and M=Pd(II),Pt(II) , Ag(II))and [Ag2(L)4NiCl2].
2-[M(L)3][M=Au(III)]in addition to the complexes
[Au(L)3(1,10 –Phen)] .
II-The addition reactions resulted in the formation of the complexes [M(tds)Cl2] whene Pt(II).The prepared complexes were characterized using molar conductivity, UV-Vis and IR spectra in addition to magnetic measurements and metal analysis by atomic absorption .The results suggest a tetra-or hexa-coordinated complexes and also displayed the importance of using different solvents upon the type of reaction and prodect.

Keywords: Diaminothiuramdisulfide, Metals, Coordinated complexes

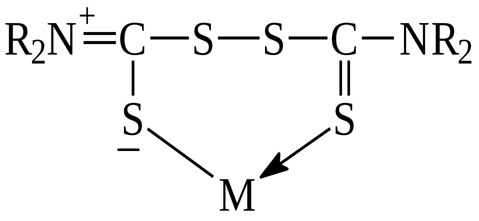
Introduction

Thiuramdisulfide compounds are one of the most important disulfide compounds known to have the formula [RR-NC(S)S]2 As R=R- alkyl or aryl is called tetra- alkyl or aryl thiuramdisulfide R4tds, which is derived from thiuramsulfide, known as BiS (N,N-dialkyl Thiucarbamol sulfide is the ester thiucarbamoyl for thiucarbamic acids These compounds are bio-effective(1) and when it is n=2) it is known as the (R4tds) and are antifungals that affect plants In past centuries, heterogeneous ring compounds have gained special attention in medical chemistry because they have antibacterial(2) and fungal properties, particularly potatoes and tomatoes(3,4), and in the process of accelerating the rubber accent(5,6), oxidative resistance, oxidization resistance and preventing the removal of the color from the rubber(7). In medicine, thiuram complexes use disulfide in the treatment of alcoholics(8) and have been found to be anti-virus-leading to HIV,such as AIDS(9). Thiuram disulfide ligands are the only one within thiolito ligands capable of forming the thiocarbamate ligands by breaking the sphincter (SS) in the reduction process. Thiocarbamate has the ability to spread the positive charge of the metal to the outer surface of each complex(10,11). In terms of consistency, these ligands are characterized by their compatibility with a number of transition metals, such as chelated bidentate sulfides through the two sulfur atoms.

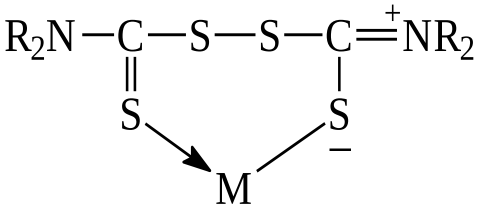
- Selection and peer-review under responsibility of the Organizing Committee of the Conference



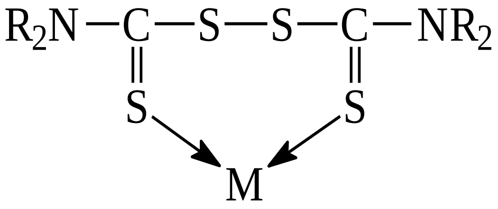
(Ia



(Ib



(Ic



(Id

Some methods of preparation for thiuramdisulfide ligand and their complexes, Because these ligands are important, we know the methods of their preparation:

1) Indirect oxidation method:

Thiuramdisulfide compounds are prepared by oxidizing the thiocarbamate compounds using an oxidizing agent such as potassium ferrocyanide [K_3 [Fe (CN) $_6$]) $^{(10,12)}$according to the following formula

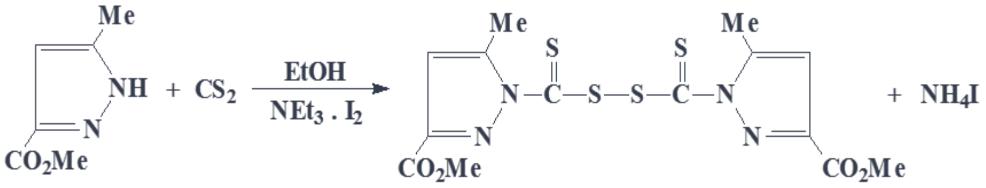
$$2\,RNHCS_2Na + 2\,K_3[Fe(CN)_6] \longrightarrow RNH-\overset{S}{\overset{\|}{C}}-S-S-\overset{S}{\overset{\|}{C}}-NHR + 2\,NaK_3[Fe(CN)_6]$$

Hydrogen peroxide (H_2O_2) , sodium tetrachloride [$Na_2S_4O_6$] or bromine cyanide (BrCN) in ethanol or iodine (I_2) as in the equation:

$$2\,R_2NCS_2Na + I_2 \longrightarrow R_2N-\overset{S}{\overset{\|}{C}}-S-S-\overset{S}{\overset{\|}{C}}-NR_2 + 2\,NaI$$

2) Direct Oxidation method:

Thiuramdisulfide compounds are prepared directly from the reaction of the secondary amine R_2NH with carbon dioxide CS_2 in the presence of I_2 and one of the amino bases such as pyridine, or triethylamine, as in the following equation:



3)The thiocarbamate complexes are oxidized using one of the halogens (X_2).

In 2004(13) , heterogeneous quad-core complexes for tin metal (IV) formula [Sn (L) 3I (PPh3) 2 (M`Cl2) 3] were prepared as M` = Cu (II) and Co (II). Ni (II), L = H2NNHCS2 and PPh3 = triphenylphosphine, as shown in Figure .

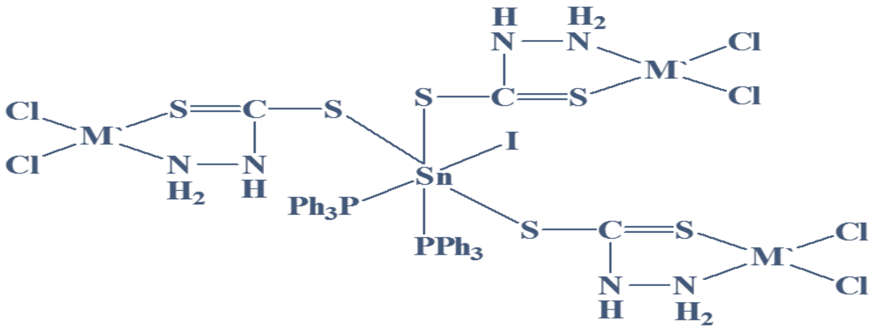


Figure of Complex $[Sn(L)_3I(PPh_3)_2(M`Cl_2)_3]$

The purpose of the research

The research aims to compare the number of (free) metals transition to the elements of the (VIII) group as well as the elements (IB) with the chlorides of these elements its ability to degrade one of the compounds (diaminothiuramdisulfide) to the dithiocarbamate ion to form complexes of the transition metals used in addition to a simple study of the effect of the solvent factor on the process of interaction and outputs of reactions.

Method

Preparation of ligand aminodithiocarbamate ammonium (NH_4L)

Added (6.04 ml,0.1 mol) of carbon disulfide(CS_2) gradually with cooling and constant stirring to (5 ml,0.1 mol) of hydroxyin water($NH_2NH_2.H_2O$). It turns into a white dough slanted to yellow and then filters, washed and re-crystallized**.**

Preparation of ligand aminothiuramdisulfide(tds)

Add (3.95 g,0.012mol) of potassium ferrocyanide $K_3[Fe(CN)_6]$ dissolved in (15 ml) of water to (1.25 g,0.01mol) of amino dithiocarbamate ammonium above and dissolved in an equal amount of water and ethanol and the addition is gradually done in an ice bath where yellow deposits are formed. Green and has been able to obtain a dithiuramdisulfide compound (tds) using I_2 dissolved in ethanol.

Preparation of Na_2PdCl_4 palladium salt solution(14).

The heating of equal amounts of palladium chloride salt ($PdCl_2$) and NaCl is brought in by a mollet ratio (2:1 in 5 ml of distilled water until palladium chloride dissolves and a red-brown solution is formed.

Preparing K_2PtCl_4 Platinum salt(15)

Melts 15 g of platin metal in 320 ml of royal water, climbs the mixture for at least(14 hours) to obtain H_2PtCl_6 acid, dissolves the resulting acid in 200ml of distilled water and is added a solution prepared from dissolved (6.4g) of potassium chloride in (60ml) of distilled water to deposit the complex (K_2PtCl_6) yellow color, filtered and washed with cold water and dried.3g dissolved from hydrochloride hydrazine ($N_2H_4.HCl$) prepared from the addition of concentrated hydrochloride acid to hydrochloride (N_2H_4). H_2O) drop-drop to be completed white deposit formation in 70 ml of distilled water and added to (20.5g) of complex K_2PtCl_6 heats the mixture to boil for half an hour to get a solution of a dark red color. For the fractional platinum, the solution cools down in the form of wild red crystals by 75%. (K_2PtCl_4)

Preparation of complexes with formulas [M $(L)_2$](M= Ag,Pd,Pt)

Add the ligand solution of tds (1.07gm,0.005mol) dissolved in 30 ml of dry toluene and climbs the mixture with constant stirring using a magnetic motor in a 14-hour glass ring with 0.539 g of silver metal or 0.717gm of AgCl and 0.975 g of platinum metal and the complex palladium was obtained using 1.472 of Na_2PdCl_4 paladium salt.

Preparation of [Au (L)$_3$]

Add(0.985gm) of gold metal is added with(1.605 g,0.0075 mol) from the diaminoThiuramdisulfied with 30 ml of dry toluene and using a thermal escalation and thus the complex composition.

Preparation of [Pt (tds)Cl$_2$]complex

Add(1.07gm,0.005mol) of tds and 20 ml dissolved compound are added in(THF) with 2.076 g of K_2PtCl_4 salt that climbs the reaction mix with continuous stirring for 2 hours until complex formation**.**

Preparation of [Au (L)$_3$ (1,10Phen)] complex

Add (1.969 g,0.01mol) of gold metal in pieces (3.210 g,0.015 mol) of diaminothiuramdisulfide and dissolved in (20ml) of dry toluene, the mixture climbs with constant stirring for 15 hours as it forms a dark green deposit and dries. Melt (5.179 g,0.01mol) from the complex prepared in 20 ml of chloroform and then added to (1.802 g,0.01 mol) of(1,10 phen) dissolved in 10 ml of methanol climbs the mixture as it filters a greenish blue deposit and dries.

Preperation of [Ag$_2$(L)$_4$NiCl$_2$]

Add (0.717 g, 0.005 mol) anhydrous silver (I) chloride (AgCl) is added to (1.070 g, 0.005 mol) of the diaminothiuramdisulfide compound dissolved in (20 ml) of tetrahydrofuran (THF). The mixture is stirred with constant stirring using a magnetic motor in a 50 mL glass flask for 2 hours, the precipitate is filtered and dried. Dissolve (1.609 g, 0.005 mol) of the above prepared complex in (20 ml) chloroform and add (0.324 g, 0.0025 mol) of nickel anhydrous (II) chloride ($NiCl_2$) dissolved in (20 ml) of dimethyl sulfoxide (DMSO). The mixture ascends with constant stirring, forming a shiny dark blue precipitate, filtered and dried.

Results and Discussion

Table 1.Analytical data and Physical Properities of ligand and their

No	Compounds	Color	M.P(ºC)	Yeild%	M%	Λm(ohm^{-1} mol^{-1} cm^2)	μ eff. (B.M)
L1	$NH_4L(H_2NNHCS_2NH_4)$	Whitish yellow	125	70			
L2	$H_2NNHC(S)SSC(S)NHNH_2$ (tds)	Yellowish green	155	78			
1	[Pd(L)$_2$]	Green	198	58	-	3	Dia
2	[Ag(L)$_2$]	Yellow pall	161	68	33.51 33.48	4	1.72
3	[Pt(L)$_2$]	Greenish yellow	159	62	47.68 47.60	10	Dia
4	[Au(L)$_3$]	Dark green	186	75	38.02 37.22	18	Dia
5	[Pt(tds)Cl$_2$]	Brownish yellow	190	67	40.63 40.71	7	Dia
6	[Ag$_2$(L)$_4$NiCl$_2$]	Dark blue	182	67	27.89 27.99	6	2.05
7	[Au(L)$_3$(Phen)]	Bluish green	173	71	28.21 28.14	17	Dia

Λm= Molar Conductivity , μ eff= effective magnetic moment , M.P= melting point

The magnatic moment data of these Complexes Calculated from the corrected magnatic susceptibilities determined at 25 ºC are given in (Table-1). It was found that the complexes of palladium and platinum(1,3,5), which have tetra coordination arrangement with low-consistency, have magnetic moment (Dia) qualities(16). Magnetic measurements of gold complexes (III) recorded (4 and 7) for the complex >have shown (Dia) properties that are similar to platinum (II) and are consistent with the magnetic moments found in literature(17). Magnetic measurements of the silver complexes (II) (2 and 6) above showed magnetic moment (1.72 and 2.05) respectively and these values are consistent with the magnetic moment of torque values of a single electron perpenduation.

The palladium (II) and platinum(II) complexes with the shape of the square planner have three electronic transitions allowed(16),The electronic spectrum shows strong bands at(15000-23000cm^{-1})when they return to the transition($^1A_1g \longrightarrow {}^1A_2g$) ,(24000-29000cm^{-1}) Attributable to the transition($^1A_1g \longrightarrow {}^1B_1g$) and appear some complexes third band ($^1A_1g \longrightarrow {}^1Eg$) at different high ranges. The electronic spectrum showed of Pd(II) and Pt(II) complexes(1,3,5) absorption bands in range(16806-22831cm^{-1})when their return to the transition ($^1A_1g \longrightarrow {}^1A_2g$) And there were other packages in the range(24900-24449cm^{-1}) that are back on the transition ($^1A_1g \longrightarrow {}^1B_1g$) And the appearance of strong absorptions at the range(33112-38910cm^{-1}) may represent the third transition ($^1A_1g \longrightarrow {}^1Eg$) Mixed with charge transition(C.T)(18) in a few cases, it's due to ligand bands. Ligand transition may be displaced to the lengths of the wave length low or higher than the complexes, indicating the composition of the complexes. Through the electronic spectrum, these values are consistent with the firm values of the order of the square planner around the metal atom.

Give the electronic spectrum of the gold complex (III) recorded above absorption packages at range(15220-20576cm^{-1}) and attributable to the transition($^1A_1g \longrightarrow {}^1A_2g$) and another package at(32894cm^{-1})when returning to the transition($^1A_1g \longrightarrow {}^1Eg$) While no was observed The second package, which represents the transition($^1A_1g \longrightarrow {}^1B_1g$) is observed and the similarity is observed in the packet locations with platinum(II) complexes (above).

The electronic spectrum of silver complexes (II) similar to the copper(II)like electronic tetra coordination(square planner arrangement) shows two types of electronic transitions: ($^2B_1g \longrightarrow {}^2A_1g$), ($^2B_1g \longrightarrow {}^2Eg$). These transitions are shown in the area specified between(14000-18000cm^{-1}) and attributable to the two electronic transfers above in the form of a single package to approximate their position(19) The electronic spectrum of the prepared silver(II) complexes showed the presence of absorption packs in the range(14220-16863cm^{-1}) these values are consistent with the values of the electronic spectrum of silver complexes(II) the tetra coordination (square planner)(20,21), which are often deformed towards tetra hedral.

Table 2.IR spectra of complexes

No	υ(C-S)	υ(C=S)	υ(C=N)	υ(NH_2)	υ(M-S)	υ(M-N)	υ(M'-N)	υ(M-N phen)	υ(S-S)
L1	1010	-	1475	3454	-	-	-	-	-
L2	980	1047	1472	3451	-	-	-	--	438
1	972	1030	1477	3336	420	510	-	-	-
2	1009	-	1481	3445/3380	422	524	-	-	-
3	1001	-	1486	3415	419	-	-	-	-
4	979/998	1022	1484	3369/3440	415	523	-	-	-
5	-	996	1485	3409	409	-	-	-	437
6	982	-	1486	3360/3429	417	530	451	-	-
7	992	1028	1487	3421	419	-	-	452	-

A technique(IR) was used to study ligands and their complex prepared within the range (400-4000cm-1) as they create new coordination bands between the ligand and the atoms of the metal lead to Electronic structure and Energy level &Symmetry in ligands. in These changes affect the seismic frequencies of the ligand and therefore the seismic spectromeons(22).

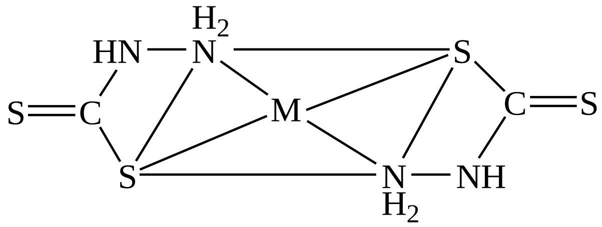
Show the spectrum(IR) of the Diaminothiuramdisulfied two absorption packs at(1047cm-1)and(980cm-1) when they return to the two groups υ(C=S)and υ(C-S) Respectively(Table-2) These beams are displaced towards the frequencies when the ligand is connected to the metal's ion By measuring the complexes(Tabel-2), A spectrum of amino dithiocarbamate ammonium was shown an absorption pack at(1010cm-1) returning to υ(C-S) . When measuring the complex(1), two absorption packs appeared at(1030,972cm-1) its packs of the two groups υ(C=S)and υ(C-S) Respectively in a sign that these complexes are linked to amono dentate by negative sulfur ion, as research published in the field has indicated (22,23,24).

The complexes(2,3,6) showed asingle band υ(C-S)in range(982-1009cm-1) A sign of the bidentate association of the thiocarbamate ligand.while gold complex(4) is appeared three bands which are two bands υ(C-S) indicative of the presence of tri-sulfur with two metal atoms in the bi molecule and one band of υ(C=S). In IR Spectra (tds) gave a weak package in(438cm-1) that belonged to the group. υ(S-S).(25) Through a(IR) measurement of the prepared complexes it was observed that a package in the complex (17) appeared in(437cm-1) this location is near to its location in the spectrum of the ligand Which indicates that as far as it is(S-S) without breaking the ligand and the link of the ligand with metal atom through group(C=S).

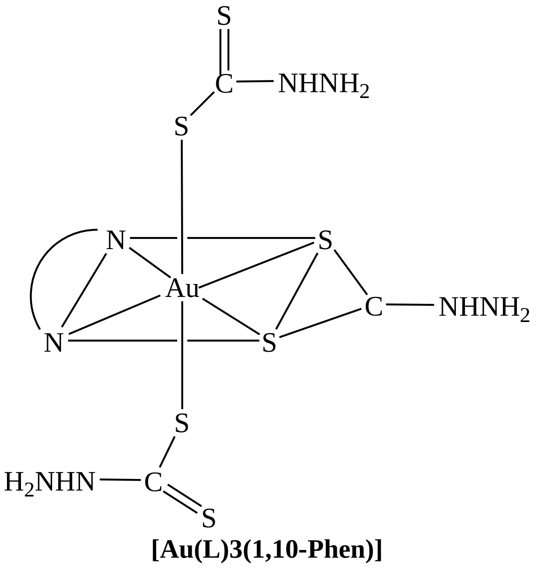
Both Ligands in the (IR) spectrum gave an absorption package at (1475,1472cm-1) respectively and these bands returen to the molecular double bonds.(26,27)(C N) This value lies between the frequency of the single and the double bonds. When complexes are formed, frequency values are displaced to high frequencies in the range(1477-1487cm-1).

Vibrations υ(M-N) appeared in the complexes(1,2,4,6)at range(510-530cm-1), indicating that metal atoms were associated with the nitrogen atom in group(NH2)(Table2)While The Complex(6)is appeared band υ(M'_N)at(451cm-1) This is consistent with what he said(Nakamoto)(28), and in this area, the nickel metal has been confirmed in contact with the ligand nitrogen(29).

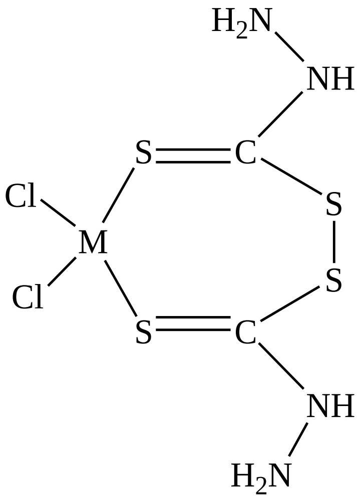
The complex (7) gave a pack of absorption to the insistent(M-N-phen)at(452cm-1) The firmness packets generally appear at the range (360-500cm-1)(28).



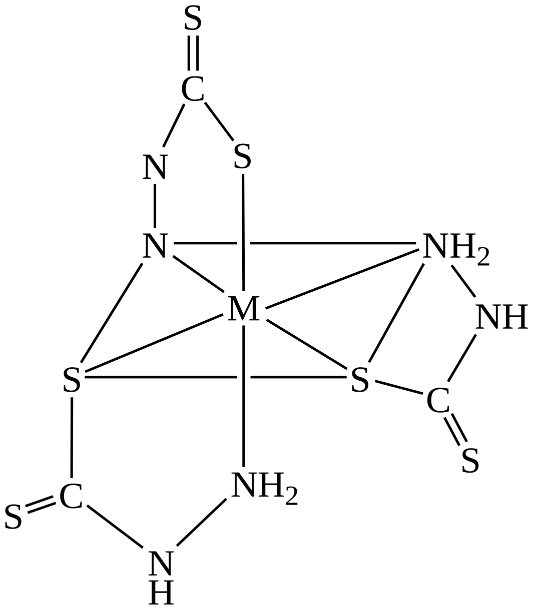
$[M(L)_2]$ (M=Pd, Pt, Ag)



[Au(L)3(1,10-Phen)]



[Pt(tds)Cl$_2$]



[Au(L)$_3$]

References

Angeli, E., Wagner, J., Lawrick, E., Moore, K., Anderson, M., Soderland, L., & Brizee, A. (2010, May 5). General format. Retrieved from http://owl.english.purdue.edu/owl/resource/560/01/

Calfee, R. C., & Valencia, R. R. (1991). APA guide to preparing manuscripts for journal publication. Washington, DC: American Psychological Association.

Duncan, G. J., & Brooks-Gunn, J. (Eds.). (1997). Consequences of growing up poor. New York, NY: Russell Sage Foundation.

Harlow, H. F. (1983). Fundamentals for preparing psychology journal articles. Journal of Comparative and Physiological Psychology, 55, 893-896.

Helfer, M. E., Kempe, R. S., & Krugman, R. D. (1997). The battered child (5th ed.). Chicago, IL: University of Chicago Press.

Henry, W. A., III. (1990, April 9). Making the grade in today's schools. Time, 135, 28-31.

Lastname, F. N. (Year). Title of dissertation. (Doctoral dissertation). Retrieved from Name of database. (Accession or Order Number)

Lastname, F. N. (Year). Title of dissertation. (Unpublished doctoral dissertation). Name of Institution, Location.

O'Neil, J. M., & Egan, J. (1992). Men's and women's gender role journeys: A metaphor for healing, transition, and transformation. In B. R. Wainrib (Ed.), Gender issues across the life cycle (pp. 107-123). New York, NY: Springer.

Plath, S. (2000). The unabridged journals. K. V. Kukil (Ed.). New York, NY: Anchor.

Schnase, J. L., & Cunnius, E. L. (Eds.). (1995). Proceedings from CSCL '95: The First International Conference on Computer Support for Collaborative Learning. Mahwah, NJ: Erlbaum.

Schultz, S. (2005, December 28). Calls made to strengthen state energy policies. The Country Today, pp. 1A, 2A.

Scruton, R. (1996). The eclipse of listening. The New Criterion, 15(30), 5-13.

Author Information

Afyaa M. Younus
University of Mosul
Mosul, Iraq
Contact E-mail: younis1986mmyy@yahoo.com

Ihsan A. Mustafa
University of Mosul
Mosul, Iraq