Preparation , Characterization and Radiolysis of Some Copper(II) With Mixed Ligand Complexes

Z.F. Dawood[1] **and Y.T. Mahmood**

1 Department of Chemistry, College of Education, University of Mosul, Mosul, Iraq

Abstract:

Copper (II) complexes with mixed ligands : benzIl bis(semicarbazone)- $BSCH_2$ and substituted salicylic acid (salicylic acid - A_1H or 2-acetylsalicylic acid - A_2H or 3,5-dinitrosalicylic acid - A_3H or 5-aminosalicylic acid - A_4H or 5-sulphosalicylic acid - A_5H) have been prepared and characterized by physical and chemical methods . Complexes of the type $[Cu(BSCH_2)(AH)](NO_3)_2$ and [Cu(BSCH)(A)] (where AH = A_1H or A_2H or A_3H or A_4H or A_5H, A = deprotonated AH ligand and BSCH = deprotonated $BSCH_2$ ligand) have been proposed in neutral and basic medium, respectively. Under conditions where hydroxyl radicals scavenged by formate (in presence of nitrogen gas), the results observed indicated that a reduction process involving copper ion may occurred. Moreover, the so formed $CO_2^{\cdot-}$ under these conditions reduced Cu(II) to Cu(I) . The conductivity and electronic spectral measurements were in a good agreement with the above . The conclusion depending on our results, concerning the existance of charge transfer between metal and ligand in the complexes.

Key Words : Copper complexes mixed lignads, semicarbazone, substituted salicylic acid, Radiolysis.

Introduction:

Semicarbazone ligands bonding through the nitrogen and oxygen atoms to the central metal ions formed an important class of biologically active ligands[1] and provided models for metal-ligand bonding sites in several enzymes[2] . In biological systems, the enzymes are frequently strongly dependent on the presence of small amounts of metal ions. Semicarbazone complexes of some transition and non-transition elements have been reported[3-5] .

Mixed ligands complexes have been studied for transition and non-transition metal ions due to their important role in biological processes[6,9]

The historical uses of copper and it's certain copper complexes for the treatment of radiation sickness and more recently as an adjunct to radiotherapy for cancer patients[10,11] .Many cellular components undergo radiolysis when exposed to gamma rays. Water represent 70% of the human body mass gave the following products :

$$H_2O \rightsquigarrow e^-_{aq}, H^\cdot, {}^\cdot OH, H_3O^+, H_2, H_2O_2$$

Since some complexes are involved in biological systems though some of these system involved reducing free radical . The hydrated electron e^-_{aq} and hydrogen atom ($H^\cdot$) have capable to reduce the central metal ion[10] . There has been considerable interest, recently, in the radiolytical study of copper(II) complexes[12,13] .

To the best of available knowledge, the preparation and characterization of new copper (II) complexes containing mixed ligands {benzil bis(semicarba- zone) and substituted salicylic acids A_1H, A_2H, A_3H, A_4H and A_5H} and the effect of gamma irradiation on such complexes have not yet been reported . It is a matter of interest to determine the extent to which gamma irradiation for these new complexes would be affected.

Experimental:

I. Analytical and physical measurements :

Copper ion contents have been determined by applying standard method[14,15] .

Conductivity measurements have been carried out with an electrolytic conductivity measuring set LF-42 and Multiline F/SET-Z WTW Wissenschaf using 10^{-3} M dimethylformamide solution at 25 ^{0}C . The infrared spectra has been recorded on a Pye - Unicam 1100 Infrared Spectrophotometer in the 400 - 4000 cm^{-1} range using KBr pellets . Electronic spectra has been recorded on Shimadzu UV-210A Spectrophotometer and Ultraviolet-Visible Spectrophoto- meter Cecil-1021 for 10^{-3} M solutions of the ligands and their complexes in dimethylformamide at 25°C, using a 1 cm cell . Magnetic susceptibility of the complexes have been measured by Bruker B.M6 . Molecular weights of the ligands and the complexes have been determined cryoscopically[16] .

II. Synthetic Methods :

Benzil bis(semicarbazone) $BSCH_2$ has been prepared according to literature method[17] .

A general procedure has been adopted for the preparation of the complexes in neutral and basic medium. In neutral medium, a solution of 1g (0.0041 mole) of copper nitrate.$3H_2O$ in 5 ml. water has been added to the solution of 1.23g (0.0041 mole) of benzyl bis(semicarbazone) and one of the carboxylic acid (salicylic acid , 5-aminosalicylic acid, 3,5-dinitrosalicylic acid, 2-acetylsalicylic acid and 5-sulphosalicylic acid : 0.0041 mole – the amounts in grams are listed in Table 1). The mixtures have been refluxed for three hours followed by evaporation to the half their volumes then cooled to room temperature . The products were separated by filteration, washed with petroleum ether (60^0, 80^0) and dried . In basic medium, complexes have been prepared by applying same amounts used in neutral medium, after mixing the metal salts with the ligands and heating on a water bath, potassium hydroxide solution (1M) has been added until pH of the solutions were 8-9. The mixtures have been heated on a water bath for half an hour then allowed to stand then cooled. The products are filtered off and washed with petroleum ether (60^0, 80^0) and dried .

Table 1 : Amonuts , physical and analylical results

No	Complex	Wt of AH (g)	Medium	% yield	Color	m.p or d* ^{0}c	^$_M$ **	Cu Calc./ (obs.)	M.Wt Cal./ (obs.).	μ$_{eff}$ BM
1	$[Cu(BSCH_2)(A_1H)](NO_3)_2$	0.5714	Neutral	94.48	Olive	210d	134.0	9.20 (9.78)	649.5 (625.0)	2.0
2	$[Cu(BSCH)(A_1)]$	0.5714	Basic	97.52	Green	202	25.0	12.13 (11.80)	523.5 (490.0)	1.9
3	$[Cu(BSCH_2)(A_2H)](NO_3)_2$	0.7453	Neutral	96.70	Olive	170d	147.7	9.18 (8.80)	691.5 (681.0)	1.7
4	$[Cu(BSCH)(A_2)]$	0.7453	Basic	97.32	Pale Brown	200d	21.0	13.64 (12.90)	565.5 (533.0)	1.7
5	$[Cu(BSCH_2)(A_3H)](NO_3)_2$	0.9441	Neutral	94.11	Yellowish-green	168d	146.7	8.59 (8.00)	739.5 (681.0)	1.8
6	$[Cu(BSCH)(A_3)]$	0.9441	Basic	97.08	Pale green	186d	26.0	10.35 (10.00)	631.5 (584.0)	1.8
7	$[Cu(BSCH_2)(A_4H)](NO_3)_2$	0.6335	Neutral	95.57	Brown	158d	150.0	9.56 (9.10)	614.5 (584.0)	1.8
8	$[Cu(BSCH)(A_4)]$	0.6335	Basic	97.43	Black	194d	29.0	11.79 (11.40)	538.5 (533.0)	1.9
9	$[Cu(BSCH_2)(A_5H)](NO_3)_2$	0.9027	Neutral	96.55	Green	103	136.0	8.70 (9.20)	729.5 (681.0)	2.1
10	$[Cu(BSCH)(A_5)]$	0.9027	Basic	96.19	Brown	125	29.0	10.52 (11.10)	603.5 (584.0)	2.0

* d = decomposition temperature ** ^$_M$ = molar conductivity in ohm^{-1}cm^2 mol^{-1}

III. Radiolysis of the Complexes :

All the solutions (10^{-4} M) of the metal salt, ligands and complexes were prepared using 10^{-3} M formate solution in triply distilled water (neutral medium) or 10^{-3} M formate and 10^{-1} M sodium hydroxide solution in triply distilled water (basic medium) . The solutions were saturated with nitrogen gas.

All gamma irradiations have been carried out using gamma cell-220 perchased from the Canadian Atomic Energy. The absorbed dose has been determined using Fricke dosimeter[18] . The does rate was 2.7×10^{16} eV.ml^{-1}min^{-1}.

Results and Discussion:

The reaction of copper(II) nitrate, benzyl bis(semicarbezone) and the carboxylic acids in 1:1:1 molar ratio in both neutral and basic medium can be represented by the following reactions :

$Cu(NO_3)_2.3H_2O + BSCH_2 + AH \rightarrow [Cu(BSCH_2)(AH)](NO_3)_2 + 3\,H_2O$ (in neutral med.)

$Cu(NO_3)_2.3H_2O + BSCH_2 + AH + 2KOH \rightarrow [Cu(BSCH)(A)] + 2KNO_3 + 5H_2O$(in basic med.)

(where AH = any one of the carboxylic acid A_1H or A_2H or A_3H or A_4H or A_5H ; A= deprotonated carboxylic acid, $BSCH_2$= benzyl bis(semicarbazone) ; $BSCH^-$ = deprotonated $BSCH_2$) .

The resulted complexes are colored solid, slightly soluble in water, ethanol and soluble in dimethylformamide . Copper ion contents and molecular weight determination[14,16] revealed that the complexes have the composition $[Cu(BSCH_2)(AH)](NO_3)_2$ and $[Cu(BSCH)(A)]$ in neutral and basic medium , respectively (Table 1) . The molar conductivities of the complexes in 10^{-3} M dimethyl- formamide are determined, the values shown in Table 1 approach those expected for 1:2 and non electrolytes[19] for complexes prepared in neutral and basic medium, respectively .

The room temperature (25 ^{0}C) magnetic moments of copper (II) complexes are in the range of 1.7-2.1 B.M. (Table 1), indicating the presence of one unpaired electron and assigned to a monomeric structure having distorted octahedral geometry[20,21] (Table 2).

Table 2 : IR spectral data of the ligands and their complexes (Values in Cm^{-1})

Comp.	υC=N Semi	υNH$_2$ Semi	υC=O Semi	υC-O Semi	υ$_{COO^-}$ (s)*	υCOO$^-$ (as)**	Δυ	υNH υO-H acid	υCu-N	υCu-O
BSCH$_2$ AH	1610	1455	1700		1375-1390	1575-1595	200-205	3200-3300 3500-3600		
1	1510	1455	1640		1400	1580	180	3200-3300 3500-3600	550	725,650
2	1530	1455		1230	1370	1550	180	3500-3600	600	650,750
3	1520	1455	1630		1380	1550	170	3200-3300 3500-3600	500	675,720
4	1540	1455		1275	1360	1540	180	3500-3600	500	650,750
5	1510	1455	1650		1390	1570	180	3200-3300 3500-3600	550	625,700
6	1520	1455		1230	1380	1550	170	3500-3600	550	650,700
7	1530	1455	1640		1400	1580	180	3200-3300 3500-3600	500	650,720
8	1530	1455		1230	1400	1570	170	3500-3600	500	650,700
9	1520	1455	1650		1390	1540	150	3200-3300	575	650,750
10	1515	1455		1240	1360	1530	170	3500-3600	600	600,700

- s = symmetry ; ** as = asymmetry

The infrared spectra of semicarbazone ligand showed a strong band at 1610 cm^{-1} which is attributed to C=N group shifted towards a lower frequency on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation[3,22,23] . The next strong band at 1700 cm^{-1} which is attributed to C=O group . This value shifted towards a lower frequency on coordination, in neutral medium, indicating the formation of chelation between the oxygen of the C=O group and the metal ion[22,24,25] . Meanwhile, in basic medium , this bond was disappeared in the complexes and a new band has been observed at 1400 cm^{-1} due to bending enolic OH establishing coordination of the ligand through the enolic oxygen atom[3,23,25] . The appearance of strong bands at 1630-1635 cm^{-1} and 1570-1580 cm^{-1} which are attributed to $\upsilon_{C=N}$ + $\upsilon_{O-C=N}$ and azine chromophore C=N-N=C, respectively, support the formation of enolic structure in basic medium[26] . The position of the ligand in the range 3200-3300 cm^{-1} due to υ_{NH} , the broadening of this band was a consequence of hydrogen bonding phenomenon. On complexation, this phenomenon is more complicated due to different factors[3,23,27,28] such as the effect of hydrogen bonding (the breaking of hydrogen bonding on complexation causes high shift to υ_{NH}) and the effect of coordination (which causes shift to lower frequency) and also the presence of other groups (NH_2 , OH) appeared in the same position. This band, however is remained unaltered in the complexes prepared in neutral medium indicating that there is no coordination through the NH group . Meanwhile in basic medium, because of the presence of hydrogen bonding it is more difficult to notice the absence of NH group, but it is well known that this band is disappeared in basic medium[3,23,27,28] due to the enolic form . The other strong bands at 3390, 3410 cm^{-1} and 1450 cm^{-1} due to υ_{NH2} and δ_{NH2} , respectively[3,22,27,28] . These bands remained unaltered on complexation indicated there is no coordination through this group and metal ion .

The spectra of carboxylic acids (Figure 1) showed a wide bands in the region 3500-3600 and 2900 cm^{-1} due to the stretching vibration of carboxylic OH, phenolic OH, respectively, this wide range is due to the hydrogen bonding . In the spectra of the complexes it is more difficult to observe the coordination due to the presence of different groups and hydrogen bonding . Whatever, in the complexes prepared in neutral medium this wide band is shifted to lower frequency Whereas for complexes prepared in basic medium it is very difficult to observe the disappearance of this band, but it is well known that this band is disappeared due to the deprotonation of the acid and formation of ionic form[24'27'29'301. The other two bands observed at 1375-1390 cm-1 and 1575-1595 cm-1 are due to the symmetric and asymmetric stretching frequency of carboxylic group, respectively . On complexation these bands are shifted to 1360-1400 cm-1 and 1530-1580 cm-1, respectively[27'31] . The difference between the symmetry and asymmetry stretching vibration for CO2- group (Δυ = 150-180 cm-1) gives indication about the manner of coordination of carboxylic group, this value showed that the carboxylic acid coordinate through CO2- group which is acted as monodentate . The infrared spectra of A2H showed a band at 1730 cm-1 due to υc=o group of acetate group[24'27]. This band is remained unaltered in the complexes indicating that there is no coordination through this group .

The complexes in neutral medium showed a band at 1385 cm-1 due to the ionic bonding of N03- group[27'31] . Whereas, the complexes prepared in basic medium did not show this band indicating the absence of NO3- group .

On the other hand the spectra of all the complexes showed new bands at 500-600 and 600-750 cm-1 due to υM-N and υM-O , (Figure 1) respectively'27'321 . The presence of these bands strongly support the formation of the complexes under investigation.

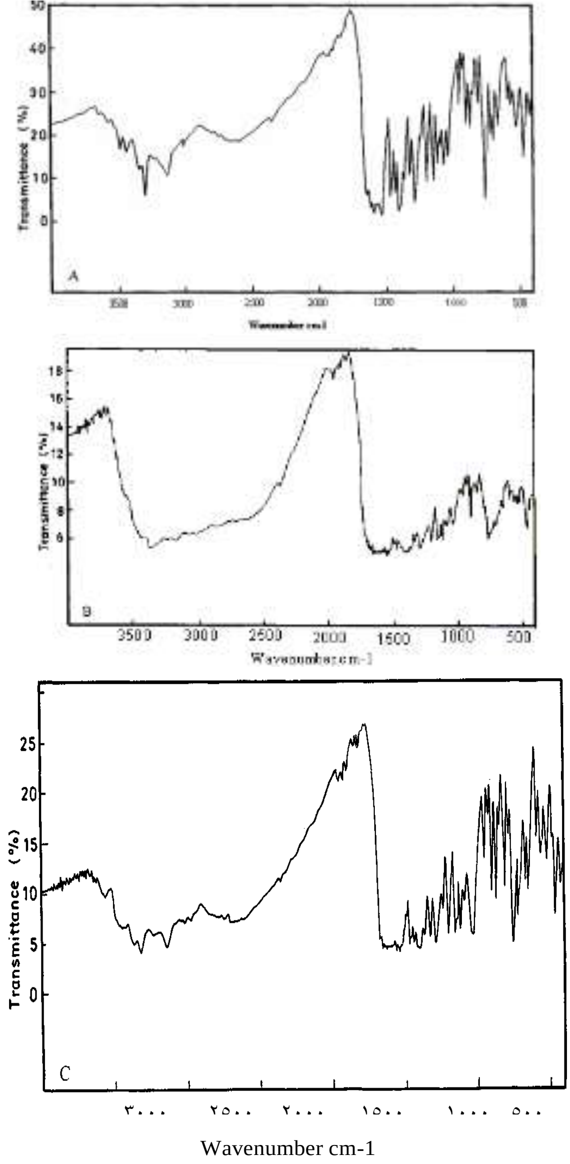

Figure 1 : Infrared spectra of : A = the ligand $BSCH_2$; B= the ligand A_2H; C= the complex $[Cu(BSCH_2)(A_2H)I(NO_3)_2$

The electronic spectra of the complexes(Table 3), showed one broad band center- ed at 13888-14285 cm^{-1}, this broad band was due to two or three transitions $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2A_{1g}$[33] . This band is comparable both in position and width with the earlier reported octahedral complexes . Since the eg^3 states have high- ly affected by Jahn Taller effect, therefore, copper(II) have distorted octahedral geometry in these complexes[34] .

Table 3 : Electronic spectral data of the complexes

No.	**C.T(Cm^{-1})**	**υ (Cm^{-1})**	**10Dq**	**C.F.S.E**
1	32100	13888	13888	8332.8
2	32000	13888	13888	8332.8
3	28900	14084	14084	8450.4
4	28600	14084	14084	8450.4
5	33100	14285	14285	8571.0
6	32800	14285	14285	8571.0
7	29000	14285	14285	8571.0
8	31100	13986	13986	8391.6
9	33000	13888	13888	8332.8
10	32900	13888	13888	8332.8

The radiolysis of water[10,11] may be described as follows:

$H_2O \rightsquigarrow (H_2O^*, H_2O^+, e^-) \rightarrow .OH , H^. , e^-_{aq} , H_2O_2 , H_2 , [H_3O^+]$

In presence of nitrogen gas and formate solution, the hydroxyl radical (.OH) and hydrogen atom ($H^.$) scavanged[10,13,35] according to the following equations :

$HCOO^- + .OH \rightarrow CO_2^{.-} + H_2O \quad (K = 2.5x10^9\ M^{-1}S^{-1})$

$HCOO^- + H^. \rightarrow CO_2^{.-} + H_2 \quad (K = 5.6x10^7\ M^{-1}S^{-1})$

The radiolysis of copper (II) nitrate (Table 4) caused a decrease in the conductivity and a change in electronic spectra at 5 min in neutral medium this may due to the following reaction :

$CO_2^{.-}/eaq + Cu^{2+} \rightarrow Cu^{+1} + CO_2$

Table 4 : Radiolytical results of copper nitrate and the ligand $BSCH_2$ in formate solution (N_2 gas) in neutral and basic medium .

	$CuNO_3$ Neutral			**$CuNO_3$ Basic**			**$BSCH_2$ Neutral**			**$BSCH_2$ Basic**		
T*	$\wedge_M \times 10^4$	λ (nm)	A	$\wedge_M \times 10^4$	λ (nm)	A	$\wedge_M \times 10^4$	λ (nm)	A	$\wedge_M \times 10^4$	λ (nm)	A
0	1.5	760 300	0.04 0.52	8.6	315	0.98	3.5	310	0.13	2.2	275	0.23
5	1.3	310	0.60	8.0	325	0.61	4.1	310	0.11	3.0	275	0.22
10	1.4	310	0.60	5.1	315	0.90	4.1	310	0.15	3.1	275	0.20
15	0.4	690 309	0.06 0.85	7.9	330	0.55	4.0	310	0.15	3.0	275	0.20
20	1.5	310	0.60	6.6	315 305	0.92 0.48	4.1	310	0.12	3.0	275	0.22
30	1.3	310	0.60	6.9	315	0.88	4.4	310	0.13	3.8	275	0.21
40	1.6	310	0.60	7.2	315	0.90	4.1	310	0.13	3.1	275	0.21
50	1.5	310	0.60	8.1	700 315	0.05 0.95	4.1	310	0.19	3.1	275	0.20
60	1.6	310	0.60	8.3	700 315	0.05 0.90	3.9	310	0.10	2.6	275	0.20

T = Time of radiation , $\wedge_M$ = molar conductivity in $ohm^{-1}\ Cm^2\ mol^{-1}$, λ=wave length , A= absorbence

Increasing the time of irradiation, conductivity was changed due to the reaction of .OH, after the consumption of formate solution, with copper (I) and forming copper (II) . Continuous irradiation caused reversible reaction.

The results in basic medium (Table 4) indicate that .OH react with OH^- forming O^{-}[11] which interact with $HCOO^-$ as follows :

$.OH + OH^- \rightarrow O^{.-} + H_2O$

$O^{.-} + HCOO^- \rightarrow OH^- + CO_2^{.-}$

and hence $CO_2^{.-}$ and e^-_{aq} reduce copper (II) to copper (I) leading to a decrease in conductivity and change in electronic spectra. Increasing time of irradiation copper (I) oxidized to copper (II) at 50 min .

The results (Tables 5-9) of gamma irradiation of the ligands in formate solution and in presence of nitrogen gas leads to a slight change in conduct- ivity and in absorbance but the wavelength is not changed except the salicylic acid. The general reaction that can happened may be represented as follow :

$L + CO_2^{.-} \rightarrow L^- + CO_2$

$L + e^-_{aq} \rightarrow L^-$

$L^- \rightarrow$ decomposition (increase in conductivity)

$L^- + L \rightarrow (L\text{-}L^-)$ association (decrease in conductivity).

Table 5 : Radiolytical results of A1H and A2H , formate solution (N2 gas) in neutral and basic medium .

	A_1H Neutral			**A_1H Basic**			**A_2H Neutral**			**A_2H Basic**		
T*	$^\wedge M \times 10^4$	λ (nm)	A	$^\wedge M \times 10^4$	λ (nm)	A	$^\wedge M \times 10^4$	λ (nm)	A	$^\wedge M \times 10^4$	λ (nm)	A
0	1.30	270	0.63	1.10	230	0.72	1.60	280	0.62	1.00	220	0.90
5	1.20	270	0.63	1.00	230	0.72	1.50	280	0.60	1.00	220	0.88
10	1.00	275	0.60	1.00	230	0.71	1.30	280	0.61	0.80	220	0.90
15	0.90	275	0.61	0.80	230	0.7	1.00	280	0.61	0.70	220	0.89
20	0.90	310 270	0.51 0.60	0.70	290 230	0.42 0.70	1.90	280	0.60	0.70	220	0.89
30	0.75	310 270	0.50 0.60	0.65	290 230	0.42 0.70	0.75	280	0.62	0.50	220	0.90
40	0.50	310 270	0.50 0.60	0.40	290 230	0.42 0.70	0.60	280	0.62	0.40	220	0.90
50	0.40	310 270	0.50 0.60	0.30	290 230	0.42 0.70	0.50	280	0.62	0.20	220	0.90
60	0.20	310 270	0.50 0.60	0.20	290 230	0.42 0.70	0.40	280	0.62	0.20	220	0.90

Table 6 : Radiolytical results of A_3H and A_4H , formate solution (N_2 gas) in neutral and basic medium **.**

	A_3H Neutral			**A_3H Basic**			**A_4H Neutral**			**A_4H Basic**		
T^*	^M×10^4	λ (nm)	A	^M×10^4	λ (nm)	A	^M×10^4	λ (nm)	A	^M×10^4	λ (nm)	A
0	2.50	300	0.60	1.10	240	0.85	2.10	270	0.8	1.7	290	0.65
5	2.50	300	0.60	1.00	240	0.85	2.00	270	0.8	1.5	290	0.65
10	2.30	300	0.60	1.00	240	0.85	2.00	270	0.8	1.2	290	0.65
15	2.50	300	0.60	1.20	240	0.85	1.80	270	0.8	1.2	290	0.65
20	2.40	300	0.60	1.10	240	0.85	1.70	270	0.8	1.0	290	0.65
30	2.40	300	0.60	1.10	240	0.85	1.70	270	0.8	0.9	290	0.65
40	2.50	300	0.60	1.00	240	0.85	1.50	270	0.8	0.6	290	0.65
50	2.50	300	0.60	1.10	240	0.85	1.20	270	0.8	0.4	290	0.65
60	2.50	300	0.60	1.10	240	0.85	1.20	270	0.8	0.2	290	0.65

Table 7 : Radiolytical results of A_5H , complex 1 and complex 2 , formate solution (N_2 gas) in neutral and basic medium .

	A_5H Neutral			**A_5H Basic**			**Complex 1**			**Complex 2**		
T^*	^M×10^4	λ (nm)	A	^M×10^4	λ (nm)	A	^M×10^4	λ (nm)	A	^M×10^4	λ (nm)	A
0	1.1	210	0.45	1.0	230	0.3	7.2	750 306	0.08 0.60	0.5	810 280	0.06 0.75
5	1.3	210	0.45	1.2	230	0.3	6.6	306	0.63	4.2	810 280	0.06 0.75
10	1.3	210	0.45	1.2	230	0.3	6.0	306	0.63	3.3	810 280	0.06 0.75
15	1.6	210	0.45	1.2	230	0.3	5.1	306	0.62	2.8	810 280	0.06 0.75
20	1.8	210	0.45	1.3	230	0.3	4.4	306	0.60	2.1	280 310	0.73 0.52
30	1.8	210	0.45	1.5	230	0.3	3.8	306 290	0.61 0.70	1.8	280 310	0.75 0.50
40	2.1	210	0.45	1.9	230	0.3	3.0	306 290	0.60 0.69	1.4	280 310	0.74 0.51
50	2.5	210	0.45	2.2	230	0.3	2.3	306 290	0.62 0.70	1.0	280 310	0.75 0.51
60	3.0	210	0.45	2.4	230	0.3	1.5	306 290	0.61 0.72	0.6	280 310	0.74 0.52

Table 8 : Radiolytical results of the complexes 3 - 6, formate solution (N_2 gas) in neutral and basic medium .

	Complex 3			**Complex 4**			**Complex 5**			**Complex 6**		
T^*	^M×10^4	λ (nm)	A	^M×10^4	λ (nm)	A	^M×10^4	λ (nm)	A	^M×10^4	λ (nm)	A
0	2.2	750 306	0.04 0.39	1.1	610 370	0.16 0.55	5.2	600 780	0.07 0.45	2.2	610 320	0.08 0.52
5	2.1	306	0.41	1.0	610 370	0.15 0.50	5.0	600 780	0.07 0.45	2.0	610 320	0.08 0.52
10	2.2	306	0.50	1.1	610 370	0.15 0.50	5.1	600 780	0.07 0.45	2.1	610 320	0.08 0.51
15	2.0	306	0.63	1.0	370 310	0.51 0.60	5.0	600 780	0.07 0.45	2.1	610 320	0.08 0.51
20	2.1	306	0.63	1.0	375 309	0.50 0.58	5.2	600 780	0.07 0.45	2.0	610 320	0.08 0.50
30	1.8	306	0.66	1.2	373 311	0.55 0.62	4.9	600 780	0.07 0.45	2.15	610 320	0.08 0.50
40	2.2	306	0.61	1.2	370 310	0.58 0.65	5.1	600 780	0.07 0.45	2.2	610 320	0.08 0.51
50	2.1	306	0.60	1.3	370 310	0.60 0.70	5.2	600 780	0.07 0.45	2.1	610 320	0.08 0.50
60	1.9	306	0.60	1.3	370 310	0.60 0.70	5.0	600 780	0.07 0.45	2.1	610 320	0.08 0.50

Table 9 : Radiolytical results of the complexes 7 - 10, formate solution (N_2 gas) in neutral and basic medium .

	Complex 7			**Complex 8**			**Complex 9**			**Complex 10**		
T*	$\wedge M\times10^4$	λ (nm)	A	$\wedge M\times10^4$	λ (nm)	A	$\wedge M\times10^4$	λ (nm)	A	$\wedge M\times10^4$	λ (nm)	A
0	6.1	650 300	0.02 1.00	4.0	600 350	0.09 0.81	6.2	730 225	0.06 0.45	4.1	810 260	0.04 0.30
5	5.9	650 300	0.02 0.90	4.0	600 350	0.09 0.83	5.8	730 225	0.06 0.45	3.5	810 260	0.04 0.30
10	5.5	650 300	0.02 0.90	3.5	600 350	0.09 0.80	5.5	730 225	0.06 0.45	3.1	810 260	0.04 0.31
15	5.0	650 300	0.02 0.90	3.1	600 350	0.09 0.85	5.0	730 225	0.06 0.45	2.6	810 260	0.04 0.29
20	4.8	650 300	0.02 0.90	2.5	600 350	0.09 0.80	4.1	730 225	0.06 0.45	2.1	810 260	0.04 0.29
30	4.0	650 300	0.02 0.90	2.0	600 350	0.09 0.81	3.2	730 225	0.06 0.45	1.7	810 260	0.04 0.30
40	3.61	650 300	0.02 0.90	1.6	600 350	0.09 0.82	2.6	730 225	0.06 0.45	1.3	810 260	0.04 0.30
50	3.0	650 300	0.02 0.90	1.0	600 350	0.09 0.80	1.9	730 225	0.06 0.45	0.8	810 260	0.04 0.30
60	2.0	650 300	0.02 0.90	0.5	600 350	0.09 0.80	1.1	730 225	0.06 0.45	1.4	810 260	0.04 0.30

The reducing radicals $CO_2^{\cdot-}$ and e^-_{aq} attack the ligand and the reduced ligand may either decomposed or associated leading to an increase or a decrease in conductivity[11,35637] , respectively.

In basic medium (Table 5-10) the $O^{\cdot-}$ react with $HCOO^-$ as indicated before . $CO_2^{\cdot-}$ and e^-_{aq} react with the ligand forming either molecular associa- tion or breakage of the ligand causes either a decrease or increase in the conductivity respectively.

Irradiation of the complexes in formate solution cause changes in conductivity and electronic spectra for complex 1, 2 , 3 and 4. This can be represented as follows :

$$[Cu^{11}(BSCH)(AH)]^{2+} + CO_2^{\cdot-}/e^-_{aq} \rightarrow [Cu^{I}(BSCH)(AH)]^{+} + CO_2$$

When the irradiation continued the conductivity and electronic spectra also changed which support the continuity of redox reaction with time irradiation[12,13,37] .

Irradiation of complexes 5 and 6 did not cause any changes in the electronic spectra and only a very slight change in conductivities which can be neglected. This supported the resistance of these complexes to the gamma radiation during the selected period time in the study.

Irradiation of complexes 7, 8, 9 and 10 cause changes in conductivity which indicate the formation of polymer which can be represented by the following equation :

$$[Cu^{II}(BSCH)(AH) \sim\rightarrow [Cu^{II}(BSCH_2)(AH)]^{\cdot} \rightarrow [Cu^{II}(BSCH)(AH)]_n$$

Conclusions:

According to the analytical, physical and spectral studies, some observations have been achieved that lead to establish the following points :

1. Benzil bis(semicarbazone) acts as tetradentate chelating ligand joint to copper (II) ion through the two azomethine-nitrogen and the two carbonyl-oxygen atoms .
2. Carboxylic acids act as bidentate chelating ligand .
3. Nitrate group present in the complexes as counter ion .
4. Copper (II) ion is probably hexacoordinated, leading to distorted octahedral geometry (Figure 2) .

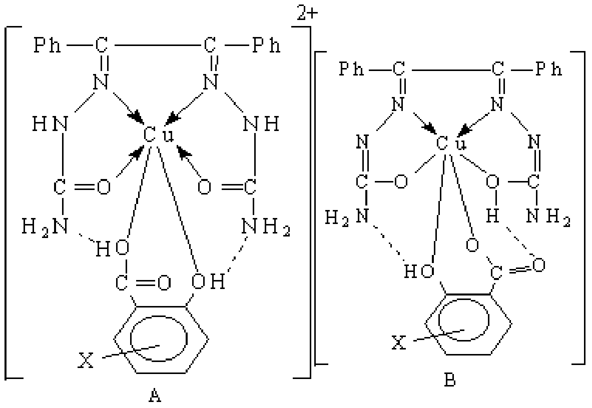

Fig. 2 : Model structure of the complexes
A=in neutral medium , B=in basic medium

5. The effect of ionizing radiation depending on some physical and spectral data causes either :

I- Decomposition of the complexes 1, 2 , 3 and 4 .
II-Complex 5 and 6 did not affected .
III-Sort of polymerization has been accompained with the radiolysis of complexes 7-10.

References :

1. B. Singh, P.L. Manrya and B.V. Agarwala; J. Indian Chem. Soc.; 59, 1130 (1982) .
2. M. Campbell, C. Elizabeth and N.R. Verno; Polyhedron; 7 (18), 1719 (1988) .
3. F. Hurta, L. Valko, M. Valko, J. SlƱma and A. Košturiak; Acta Phys. Slovaca; 51, 281 (2001) .
4. P Gupta, F. Basuli, S.M. Peng, G.H. Lee and S. Bhattacharya; Inorg. Chem.; 42 (6), 2069 (2003) .
5. A. Seyam, A. Jarrar and F. Khalili; J. Abhath Al-Yarmoak Basic Sci.; 2A, 243 (2001) .
6. J. Casas, A. Castineiras, M.C. Rodrigues-Arguelles, A. Sanchez, J. Sordo, A. Vazquez-Lopez, S. Pinelli, P. Lunghi, P. Ciancianaini, A. Bonati, P.Dall Aglio and P. Albertini; J. Inorg, Biochem.; 76 (3-4) , 277 (1999) .

7. P. Bindu, M.R.P. Kurup and T.R. Satyakeerthy; Polyhedron; 18, 321 (1998).
8. Z. F. Dawood; J. Sci & Tech.; 17, 35 (2002) .
9. P. Bindu and M.R.P. Kurup; Transition Met. Chem.; 22, 578 (1977) .
10. J.R.J. Sorenson; Chem in Britain; 170 (1989) .
11. I.J. Sallomi, A.A. Al-Obaydi and Z.F. Dawood; Raf. Jour. Sci; 13 (1), 7 (2002) .
12. Beltelheim and M. Faraggi; Radiat. Res.; 72, 71 (1977) .
13. R.M. Sellers; J. Chem. Educ.; 58, 114 (1981) .
14. A.I. Vogel,“Textbook of quantitative inorganic analysis”, Longman Inc., New York, 4th ed., 427, 463 (1981) .
15. B. Singh and H. Misra; J. Indian Chem. Soc.; 63, 840 (1986) .
16. J.W. Danials, “Experimental physical chemistry”, McGraw – Hill , 6th ed., 81 (1962) .
17. A.I. Vogel,“Textbook of practical organic chemistry”, 3rd ed., Longman Green, London, 344 (1964) .
18. K.M. Ahmad; M. Sc. Thesis, Mosul University (1985) .
19. W.J. Geary; Coord. Chem. Rev.; 7, 81, (1971) .
20. B.R. Petrovic and D.M. Petrovic ; J. Coord. Chem.; 11, 239 (1982).
21. S.A. Kettle,“Coordination chemistry”, Thomas Nelson and Sons, London , 3 , 186 , 212 (1975) .
22. Y. Kumar and S.P. Tolani; Croat. Chem. Acta; 62, 73 (1989) .
23. D.D. Yin, Z.W. Wang and L. Shan; Chinese J. Chem.; 18 (3), 364 (2000) .
24. K. Nakamoto,“Infrared and raman spectra of inorganic and coordination compounds”, John Wiley and Sons, 3rd ed., New York (1976) .
25. P.K. Singh, J.K. Koacher and J.P. Tandon; J. Inorg. Nucl. Chem.; 43, 1775 (1981) .
26. N. Kanoongo, R.V. Singh and J.P. Tandon; J.Synth. React. Inorg. Met-Org. Chem.; 17 (8 &9) 837 (1987) .
27. M.W. Ibrahim; MSc. Thesis, Mosul University, 33, 42 48, 50, 52, 53 (2002) .
28. Z.F. Dawood, S.H. Hussein and M.A. Al-Shamma; Sci. & Tech. A, 12, 71 (2004).
29. G.H. Schmid, “Organic chemistry”, Mosby Inc., USA , 188 (1996) .
30. N.G. Palaskar, D.V. Jahagirdar and D.D. Khanolkar; J.Indian Chem. Soc.; 14, 134 (1975) .
31. G.A. Wilkinson, R.D. Gillard and J.A. McCleverty, “Comprehensive coordination chemistry”, Pergamon press, Oxford, England, 1st ed., Vol. 2 (1987) .
32. L. Singh, D.K. Sharma, U. Singh and A. Kumar; Asian J. Chem.; 16 (2), 577 (2004)
33. V.S. Shrivastava, C.P. Bhasin and G.C. Saxena; J. Indian Chem. Soc.; 63, 865 (1986) .
34. Gahlot, S. Sharma and R.K. Mehta; J. Indian Chem. Soc.; 63, 198 (1986) .
35. M.G. Simic, M.Z.Hoffman and N.V. Brezniak; J. Amer . Chem. Soc.; 99, 2166 (1977) .
36. I.G. Draganic and Z.D. Draganic, “The radiation chemistry of water ”; Academic Press, New York (1971) .
37. Z.F.Dawood Al-Tayy; Ph. D.Thesis, Mosul University, 92-114 (1998).

تحضير وتشخيص ودراسة التحلل الاشعاعي لعدد من معقدات النحاس (II) مع مزيج من الليكاندات

زهور فتحي داؤد[١] و يونس تركي محمود

[1]قسم الكيمياء، كلية التربية، جامعة الموصل، الموصل، جمهورية العراق

الملخص:

يتضمن البحث تحضير عدد من المعقدات الجديدة للنحاس (II) مع خليط من الليكاندات المتضمنة بنزل بس (سميكاربازون)– $BSCH_2$ والأحماض الكاربوكسيلية (حامض السالساليك – A_1H أو أورثواسيتيل حامض السالساليك – A_2H أو ٣،٥–ثنائي نيترو حامض السالساليك – A_3H أو ٥–أمينوحامض السالساليك – A_4H أو ٥–سلفو حامض السالساليك – A_5H) . شخصت المعقدات الناتجة باستخدام تقنيات فيزيائية–كيميائية مختلفة، واقترحت الصيغ $[Cu(BSCH_2)(AH)](NO_3)_2$ و $[Cu(BSCH)(A)]$ للمعقدات الناتجة في كل من المحيط المتعادل والقاعدي على التوالي (حيث $AH = A_1H$ أو A_2H أو A_3H أو A_4H أو A_5H و A = الليكاندات AH مزال منها بروتون و $BSCH$ = الليكاند $BSCH_2$ مزال منه بروتون) . تحت ظروف أكتسحت فيها جذور الهيدروكسيل بالفورمات (بوجود غاز النتروجين) ، أوضحت النتائج حدوث عملية إختزال تضّمنت أيون النحاس . إضافة إلى ذلك فإنّ تكوّن $CO_2^{\cdot -}$ تحت هذه الظروف تختزل نحاس (II) إلى نحاس (I) . ولقد جاءت نتائج التوصيلية والأطياف الإلكترونية معززة ذلك . يمكن الإستنتاج إعتماداً على النتائج الّتي تمّ الحصول عليها بوجود إنتقال الشحنة بين الفلز والليكاند في المعقّد .

الكلمات المفتاحية: معقدات النحاس ، مزيج من الليكاندات ، سميكاربازون ، حامض السالساليك المعوّض، التحلل الاشعاعي