National Journal of Chemistry, 2007, Volume 25,206-216 المجلة القطرية للكيمياء-2007-المجلد الخامس والعشرون

# Preparation , Characterization and Radiolysis of Copper(II) Complexes Containing Mixed Ligand

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(Received on 26/4 /2006) (Accepted for publication on 5/7/2006)

## Abstract

Complexes of the type $[Cu(B`SCH)(LH)]CO_3$ and $[Cu(B`SC)(L)]$ have been prepared in neutral and basic medium, respectively {where B`SCH= benzoin semicarbazone, B`SC=deprotonated B`SCH ligand, AH= one of the substituted salicylic acid : salicylic acid ($A_1H$), 2-acetylsalicylic acid ($A_2H$), 3,5-dinitrosalicylic acid ($A_3H$), 5-aminosalicylic acid ($A_4H$) or 5-sulphosalicylic acid ($A_5H$), A= deprotonated AH ligand}. The resulted complexes have been characterized physico-chemically.

The effect of gamma rays have been studied on these complexes under conditions where the hydroxyl radicals were scavenged by sodium formate solution and in presence of nitrogen gas. The electronic spectral data and molar conductivities indicated that copper (II) ion may be reduced to copper (I) and presence of charge transfer between the metal ion and the ligands in some complexes. In addition some complexes have been completely decomposed and some of them polymerized while the others did not affected during the selected time of irradiation.

## الخلاصة

حضرت معقدات ذات صيغ $[Cu(B`SCH)(AH)]CO_3$ و $[Cu(B`SC)(A)]$ في كل من الوسطين المتعادل والقاعدي على التوالي { حيث B`SCH = بنزوين سميكاربازون ، B`SC =الليكاند B`SCH مزال منه بروتون ، AH = أحد أحماض السالساليك المعوضة : حامض السالساليك ($A_1H$) أو 2-استيل حامض السالساليك ($A_2H$) أو 3،5-ثنائي نيترو حامض السالساليك ($A_3H$) أو 5-أمينوحامض السالساليك ($A_4H$) أو 5-سلفو حامض السالساليك ($A_5H$) ، A = الليكاند AH مزال منه بروتون} . شخصت المعقدات الناتجة باستخدام تقنيات فيزيائية-كيميائية .

درس تأثير أشعة كاما على هذه المعقدات تحت ظروف أكتسحت فيها جذور الهيدروكسيل باضافة فورمات الصوديوم وبوجود غاز النتروجين ، أوضحت نتائج الأطياف الالكترونية والتوصيلية المولارية بأن عملية إختزال للنحاس (II) الى نحاس (I) يمكن أن تحدث كما تم استنتاج وجود انتقال الشحنة بين الأيون الفلزي والليكاندات في بعض المعقدات . هذا اضافة الى أن بعض المعقدات تفككت تماما وبعضها قد تبلمر في حين بعضها الآخرلم يتأثر بالاشعاع .

## Introduction

A good deal of work has been reported on the preparation and structural investigation of semicarbazones and their complexes(1-3). This is due to their capability of acting as multidentate donor with the formation of either mono- or bi- or poly-nuclear complexes(4,5). In addition to their interesting ligational properties, semicarbazones and their complexes have important biological activities(6-8). A wide studies have been done on substituted salicylic acid complexes(9-11) due to their interesting ligational properties.

There has been growing interest in the formation of mixed ligands chelates involving ligands containing different donation sites such as sulfur, oxygen and nitrogen of different functional groups(12-15). On the other hand, coordination compounds with mixed ligands are of considerable importance in the field of metalloenzymes and other biological activities(16,17). Hence a large body of the coordination chemistry of mixed ligands with transition and non-transition metal ions have been reported recently(12-20). Due to the importance of mixed ligands complexes, we took a humble part in the chemistry of mixed ligand complexes and some articles have been published so on their coordination chemistry with transition and non-transition metal ions(21-24).

Copper and it's compounds have been used for the treatment of radiation sickness and more recently as an adjunct to radiotherapy for cancer patients(25). Since some complexes have been involved in biological system though some of these systems involved reducing free radicals. The hydrated electron and hydrogen atom have been capable to reduce the central metal ion(16). There has been considerable interest, recently, in the radiolysis of copper(II) complexes(26,27).

In the present work, new copper (II) complexes containing mixed ligands {benzoin semicarbazone - B`SCH and substituted salicylic acids $A_1H$, $A_2H$, $A_3H$, $A_4H$ or $A_5H$} have been prepared and characterized physico-chemically. The effect of gamma irradiation on such complexes have not yet been reported, therefore, it is a matter of interest to determine the extent to which gamma irradiation for these new complexes would be affected.

# Experimental

## Synthetic Methods :

Benzoin semicarbazone B`SCH has been prepared according to literature method(28). A general procedure has been adopted for the preparation of the complexes in neutral and basic medium.

**I- In neutral medium:** A solution of 1g ($8.1X10^{-3}$ mole) of copper carbonate in 5 ml. water has been added to the solution of 2.3968g ($8.1X10^{-3}$ mole) of benzoin semicarbazone and $8.1X10^{-3}$ mole of one of the substituted salicylic acids in 15 ml. hot ethanol (the amounts in grams were listed in Table 1). The mixtures have been refluxed for three hours followed by evaporation to half their volumes then cooled. The products were filtered off, washed with petroleum ether (60°, 80°) and dried .

**II- In basic medium:** Complexes of the type [Cu(B`SC)(A)] 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 (1.0 M) 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 were filtered off, washed with petroleum ether (60°, 80°) and dried.

## Analytical and physical measurements :

Copper contents have been determined by applying precipitation method after the decomposition of the complexes with concentrated nitric acid (29). Relative molecular weights of the ligands and their complexes have been determined cryoscopically(30).

Conductivity measurements have been carried out with Multiline F/SET-Z WTW Wissenschaf using $1.0x10^{-3}$ M dimethylformamide solution at 25 °C. The infrared spectra has been recorded on a Pye-Unicam 1100 Infrared Spectrophotometer in the range 400 - 4000 $cm^{-1}$ using KBr pellets. Electronic spectra has been recorded on Shimadzu UV-210A Spectrophotometer for $1.0x10^{-3}$ 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 .

**Radiolysis of the Complexes :**

All the solutions of the copper (II) carbonate, ligands and complexes have been prepared using $1.0\times10^{-3}$ M sodium formate solution in triply distilled water (neutral medium) or $1.0\times10^{-3}$ M sodium formate and $1.0\times10^{-1}$ 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 purchased from the Canadian Atomic Energy. The absorbed dose has been determined using Fricke dosimeter(31). The dose rate was $2.7\times10^{16}$ eV.ml$^{-1}$min$^{-1}$.

## Results and Discussion

The reaction of copper (II) carbonate, benzoin semicarbezone and the substituted salicylic acids in 1:1:1 molar ratio in both neutral and basic medium can be represented by the following reactions :

$CuCO_3 + B`SCH + AH \rightarrow [Cu(B`SCH)(AH)]CO_3$

$CuCO_3 + B`SCH + AH + 2KOH \rightarrow [Cu(B`SC)(A)] + K_2CO_3$

(where AH=any one of the substituted salicylic acid $A_1H$ or $A_2H$ or $A_3H$ or $A_4H$ or $A_5H$; A=deprotonated AH ligands; B`SCH =benzoin semicarbazone; $B`SC^-$= deprotonated B`SCH) .

The resulted complexes were colored solid, slightly soluble in water, ethanol and soluble in dimethylformamide. Copper contents and relative molecular weights revealed that the complexes had the composition $[Cu(B`SCH)(AH)]CO_3$ and $[Cu(B`SC)(A)]$ in neutral and basic medium , respectively (Table 1). The values of the molar conductivities (78-91 and 22-29 $\Omega^{-1}$ cm$^2$ mol$^{-1}$) approached those expected for 1:2 and non electrolytes(32) for complexes prepared in neutral and basic medium, respectively. The room temperature (25 °C) magnetic moments (1.3-2.2 B.M.) indicated the presence of one unpaired electron and assigned to a monomeric structure having distorted octahedral geometries(33).

The infrared spectra of semicarbazone ligand showed a strong band at 1620 cm$^{-1}$ attributed to C=N group was shifted towards a lower frequency on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation(5,34). The next strong band at 1700 cm$^{-1}$ which is attributed to C=O group shifted towards a lower frequency on coordination, in neutral medium, indicating the formation of chelation between the carbonyl oxygen and the metal ion(4,34). Whereas in basic medium, this band was disappeared in the complexes and a new band has been observed at 1430 cm$^{-1}$ due to bending enolic OH thereby establishing the coordination of the ligand through the enolic oxygen atom(4,5.34) . The appearance of strong bands at 1635-1640 cm$^{-1}$ and 1575-1585 cm$^{-1}$ attributed to $\upsilon_{C=N} + \upsilon_{O-C=N}$ and azine chromophore C=N-N=C, respectively, supported the formation of enolic structure in basic medium(4,5,34). The band observed at 3200-3300 cm$^{-1}$ assigned to $\upsilon_{NH}$ remained unaltered in the complexes prepared in neutral medium indicating that there is no coordination through the NH group, Whereas this band was disappeared in the complexes prepared in basic medium due to the enolic form(4,5). The other bands observed at 3390, 3410 cm$^{-1}$ and 1450 cm$^{-1}$ assigned to $\upsilon_{NH_2}$ and $\delta_{NH_2}$ , respectively, remained unaltered on complexation indicated the absence of coordination of this group with the metal ion(4,5).

Infrared spectra of substituted salicylic acids showed two bands at 1375-1390 cm$^{-1}$ and 1575-1595 cm$^{-1}$ assigned to the symmetric and asymmetric stretching frequency of carboxylic group, respectively. On complexation these bands shifted to lower frequencies (Table 2). The difference between the symmetry and asymmetry stretching vibration for $CO_2^-$

difference between the symmetry and asymmetry stretching vibration for $CO_2^-$ group ($\Delta\upsilon$ = 110 or 170-180 $cm^{-1}$) indicated that $CO_2^-$ group coordinated to the central metal ion in bidentate or monodentate manner(34,35), respectively. The next bands observed at 3500-3600 $cm^{-1}$ and 2900 $cm^{-1}$ assigned to the stretching vibrations of carboxylic OH and phenolic OH, respectively. On complexation, a negative shift of the order 30-40 $cm^{-1}$ were observed for these two bands in the complexes prepared in neutral medium, whereas for the complexes prepared in basic medium a negative shift were observed for only $\upsilon_{OH(ph)}$ and the disappearance of $\upsilon_{OH(carb.)}$ was observed due to the deprotonation of the acid and formation of ionic form (11,34,35). The band observed at 1730 $cm^{-1}$ in $A_2H$ ligand due to $\upsilon_{C=O}$ was shifted to lower frequency in the order 35-40 $cm^{-1}$ in the complexes (3, 4) indicating that there has been coordination through the carbonyl oxygen(34-36) with the metal ion .

The complexes in neutral medium showed a band at 1490 $cm^{-1}$ due to the ionic bonding of carbonato group(34,35). Whereas, the complexes prepared in basic medium did not showed this band indicating the absence of $CO_3^{2-}$ group.

On the other hand the spectra of all the complexes showed new bands at 500-550 and 600-720 $cm^{-1}$ due to $\upsilon_{Cu-N}$ and $\upsilon_{Cu-O}$, respectively(34-37). The presence of these bands supported the formation of the complexes under investigation.

The electronic spectra of the complexes (Table 3), showed one broad band centered at 13888-14084 $cm^{-1}$ due to the transition $^2E_g \rightarrow {}^2T_{2g}$ of $^2D$ state(38). This band has been comparable both in position and width with the earlier reported octahedral complexes. Since the eg state has been highly affected by Jahn Taller effect, therefore, copper(II) complexes had distorted octahedral geometry (38,39). 10Dq and C.F.S.E have been determined(37) depending on the energy level diagram for $d^9$ configuration (Figure 1)(40) . Since 10Dq= $\Delta_o$ = $\upsilon$(in $cm^{-1}$). The value of C.F.S.E was determined by applying the following equation :

C.F.S.E. = - ( 6x0.4x$\upsilon$) – (-3x0.6x$\upsilon$)

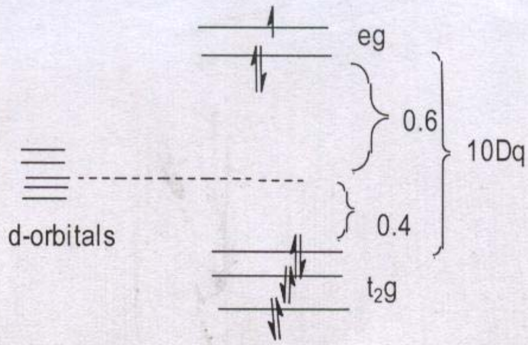

**Figure 1: Energy level diagram of Cu(II)**

Radiolysis of copper (II) carbonate in sodium formate solution and in presence of nitrogen gas for 5 min (Table 4) caused a decrease in the conductivity and a change in electronic spectra in neutral medium, this may be due to the following reaction :

$CO_2^{-}/e^-_{aq} + Cu^{2+} \rightarrow Cu^{+1} + CO_2$

Increasing the time of irradiation, the conductivity was changed which may be 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) indicated that .OH reacted with $OH^-$ forming $O^{-}$(41) which interacted with $HCOO^-$ as follows :

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

$O^- + HCOO^- \rightarrow OH^- + CO_2^-$

and hence $CO_2^-$ and $e^-_{aq}$ reduced Cu (II) to Cu (I) leading to a decrease in conductivity and change in electronic spectra. Increasing time of irradiation Cu (I) oxidized to Cu (II) at 50 min. The results of gamma irradiation of the ligands (Tables 4, 5) in formate solution and in presence of nitrogen gas have been lead to a slight changes in conductivities and in absorbance but the wavelengths have been not changed except the salicylic acid. The general reaction may be suggested as follows :

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

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

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

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

The reducing radicals $CO_2^{\cdot -}$ and $e^-_{aq}$ may have attacked the ligand and the reduced ligands may be either decomposed or associated leading to an increase or a decrease in the values of the molar conductivities(41-43), respectively. In basic medium (Table 4, 5) the so formed $O^{\cdot -}$ reacted with $HCOO^-$ as indicated before. $CO_2^{\cdot -}$ and $e^-_{aq}$ may be reacted with the ligands forming either molecular association or decomposition of the ligands which caused either a decrease or increase in the values of the molar conductivities, respectively.

Irradiation of the complexes in formate solution and in presence of nitrogen gas caused changes in conductivity and electronic spectra for complex 1-4 . This may be represented as follows :

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

$[Cu^{11}(B`SC)(A)] + CO_2^{\cdot -}/\ e^-_{aq} \rightarrow [Cu^{I}(B`SC)(A)]^{-} + CO_2$

When the irradiation continued the conductivity and electronic spectra have been changed supporting the formation of polymer(36,41-43). Irradiation of the complexes 5 and 6 did not show any changes in the electronic spectra and only a very slight changes in conductivities which could be neglected. This supported the resistance of these complexes to the effect of gamma radiation during the selected period time in the study. Irradiation of complexes 7-10 caused changes in conductivities only, indicating the decomposition of such complexes which may be represented by the following reactions :

$[Cu^{II}(B`SCH)(AH)]^{2+} \sim\rightarrow Cu^{II} + B`SCH + AH$

$[Cu^{II}(B`SC)(A)] \sim\rightarrow Cu^{II} + B`SC^- + A^-$

## Conclusions

According to the analytical, physico-chemical studies, some observations have been achieved that lead to establish the following points :

1-Benzoin semicarbazone acted as tridentate chelating ligand on coordination with copper(II) ion through the azomethine-nitrogen and the two oxygen atoms of the carbonyl and alcoholic groups .

2-Substituted salicylic acids acted as tridentate chelating ligands .

3-Carbonato group was presented in the complexes as counter ion .

4- Copper (II) ion has been probably hexacoordinated, leading to distorted octahedral geometry (Figure 2) .

5-The effect of gamma rays could be summerised as follows :

I-Reduction of the complexes 1-4, leading to the formation of polymer .

II-Complex 5 and 6 were not affected.

III-Decomposition of the complexes 7-10.

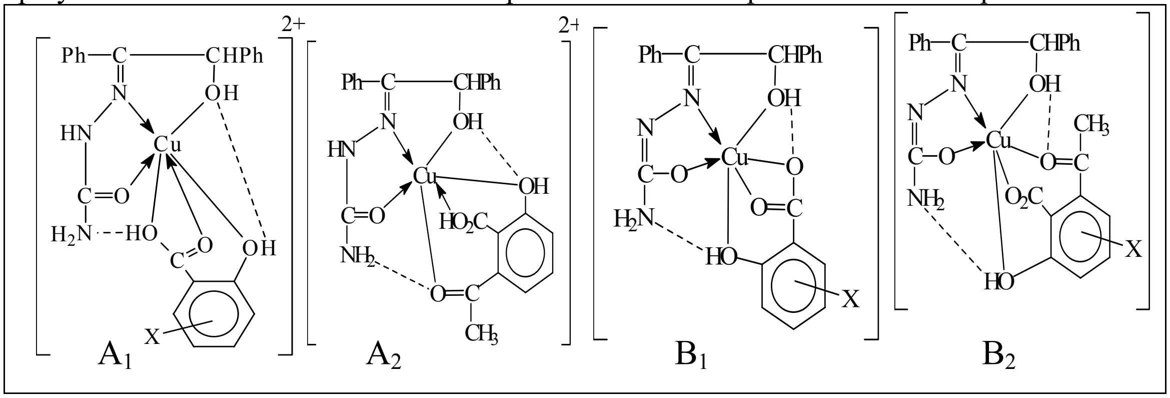

**Figure 2 : Model structure of the complexes**

$A_1$, $A_2$ = in neutral medium , $B_1$, $B_2$ = in basic medium

## Table 1 : Amounts , physical and analytical results

| No | Complex | wt of AH (g) | Medium | % yield ◘ | Color | m.p or d* $^0$c | $\Lambda_M$ ** | Cu Calc./ (obs.) | M.Wt Cal./ (obs). | $\mu_{eff}$ ● |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $[Cu(B`SCH)(A_1H)]CO_3$ | 1.1174 | Neutral | 98.14 | Brown | 109 | 82 | 11.97 (11.10) | 530.5 (490.0) | 2.1 |
| 2 | $[Cu(B`SC)(A_1)]$ | 1.1174 | Basic | 97.52 | Yellowish green | 160 | 27 | 17.23 (16.50) | 468.5 (453.0) | 2.0 |
| 3 | $[Cu(B`SCH)(A_2H)]CO_3$ | 1.4575 | Neutral | 96.03 | Olive | 106 | 78 | 9.28 (8.90) | 572.5 (533.0) | 2.1 |
| 4 | $[Cu(B`SC)(A_2)]$ | 1.4575 | Basic | 97.32 | Yellowish brown | 140 d | 29 | 13.85 (13.10 0 | 510.5 (490.0) | 2.2 |
| 5 | $[Cu(B`SCH)(A_3H)]CO_3$ | 1.8462 | Neutral | 95.78 | Yellowish brown | 110 d | 91 | 10.23 (9.50) | 620.5 (584.0) | 1.3 |
| 6 | $[Cu(B`SC)(A_3)]$ | 1.8462 | Basic | 96.11 | Yellowish green | 140 d | 26 | 13.85 (13.30) | 558.5 (533.0) | 1.8 |
| 7 | $[Cu(B`SCH)(A_4H)]CO_3$ | 1.2389 | Neutral | 97.14 | Brown | 103 d | 80 | 11.64 (11.20) | 545.5 (533.0) | 2.0 |
| 8 | $[Cu(B`SC)(A_4)]$ | 1.2389 | Basic | 97.43 | Black | 124 d | 22 | 16.56 (15.80) | 383.5 (350.0) | 1.4 |
| 9 | $[Cu(B`SCH)(A_5H)]CO_3$ | 1.7652 | Neutral | 96.89 | Pale green | 120 d | 82 | 10.40 (9.80) | 610.5 (584.0) | 1.3 |
| 10 | $[Cu(B`SC)(A_5)]$ | 1.7652 | Basic | 95.23 | Yellowish green | 178 d | 23 | 11.16 (10.80) | 448.5 (409 .0) | 1.6 |

◘ % yield = (experimental weight of the complex / theoritical weight of the complex) x 100
Theoretical weight of the complex =[(Molecular weight of complex)( weight of metal salt)] / (molecular weight of metal salt)
* d = decomposition temperature
** ^$_M$ = molar conductivity in ohm$^{-1}$cm$^2$ mol$^{-1}$
● $\mu_{eff}$ = magnetic moment in Bohr magneton

## 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 | $υ_{C-O}$ (alc.) | υCu-O | υCu-O |
|---|---|---|---|---|---|---|---|---|---|---|---|
| B`SCH AH | 1620 | 1455 | 1700 | - | 1375-1390 | 1575-1595 | 200-205 | 3200-3300<br>3500-3600 | 1250 | - | - |
| 1 | 1520 | 1455 | 1650 | - | 1410 | 1520 | 110 | 3200-3300<br>3500-3600 | 1300 | 550 | 650, 700 |
| 2 | 1520 | 1455 | - | 1250 | 1420 | 1530 | 110 | 3500-3600 | 1300 | 550 | 650, 700 |
| 3 | 1510 | 1455 | 1640 | - | 1420 | 1590 | 170 | 3200-3300<br>3500-3600 | 1300 | 500 | 650, 700 |
| 4 | 1540 | 1455 | - | 1250 | 1410 | 1590 | 180 | 3500-3600 | 1300 | 500 | 625, 700 |
| 5 | 1530 | 1455 | 1650 | - | 1410 | 1520 | 110 | 3200-3300<br>3500-3600 | 1280 | 500 | 600, 720 |
| 6 | 1530 | 1455 | - | 1275 | 1400 | 1510 | 110 | 3500-3600 | 1300 | 500 | 650, 700 |
| 7 | 1520 | 1455 | 1640 | - | 1420 | 1530 | 110 | 3200-3300<br>3500-3600 | 1300 | 500 | 650, 720 |
| 8 | 1540 | 1455 | - | 1230 | 1400 | 1510 | 110 | 3500-3600 | 1300 | 525 | 675, 710 |
| 9 | 1510 | 1455 | 1640 | - | 1420 | 1530 | 110 | 3200-3300 | 1300 | 500 | 650, 700 |
| 10 | 1520 | 1455 | - | 1230 | 1410 | 1520 | 110 | 3500-3600 | 1300 | 500 | 600, 700 |

- s = symmetric ; ** as = asymmetric

### Table 3 : Electronic spectral data of the complexes

| No. | C.T ($cm^{-1}$) | υ ($cm^{-1}$) | 10Dq ($cm^{-1}$) | C.F.S.E * |
|---|---|---|---|---|
| 1 | 32000 | 13888 | 13888 | 8332.8 |
| 2 | 31950 | 13888 | 13888 | 8332.8 |
| 3 | 32100 | 14084 | 14084 | 8450.4 |
| 4 | 32000 | 14084 | 14084 | 8450.4 |
| 5 | 34100 | 13888 | 13888 | 8332.8 |
| 6 | 34000 | 13888 | 13888 | 8332.8 |
| 7 | 29000 | 13888 | 13888 | 8332.8 |
| 8 | 28800 | 13888 | 13888 | 8332.8 |
| 9 | 31500 | 13888 | 13888 | 8332.8 |
| 10 | 31450 | 13888 | 13888 | 8332.8 |

*C.F.S.E = (6x 0.4x13888) – (3x 0.6x13888) = 8332.4 ; C.F.S.E = (6x 0.4x14084) – (3x 0.6x14084) = 8450.4

### Table 4 : Radiolytical results of $CuCO_3$ and B`SCH in formate solution ($N_2$ gas)

| | $CuCO_3$ Neutral | | | $CuCO_3$ Basic | | | B`SCH Neutral | | | B`SCH Basic | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T | $\wedge_M$ | λ (nm) | A | $\wedge_M$ | λ (nm) | A | $\wedge_M$ | λ (nm) | A | $\wedge_M$ | λ (nm) | A |
| 0 | 3.2 | 820, 710, 270 | 0.03, 0.05, 0.61 | 9.8 | 295 | 0.88 | 3.3 | 325 | 0.96 | 2.0 | 275 | 0.81 |
| 5 | 3.0 | 308 | 0.54 | 9.8 | 295 | 0.88 | 3.2 | 325 | 0.95 | 2.1 | 275 | 0.81 |
| 10 | 3.1 | 308 | 0.55 | 7.9 | 305 | 0.76 | 3.9 | 325 | 0.95 | 2.6 | 275 | 0.82 |
| 15 | 2.1 | 310 | 0.50 | 8.8 | 260, 305 | 0.68, 0.80 | 3.8 | 325 | 0.96 | 2.6 | 275 | 0.80 |
| 20 | 3.0 | 650, 310 | 0.04, 0.52 | 9.8 | 295 | 0.86 | 3.8 | 325 | 0.94 | 2.6 | 275 | 0.80 |
| 30 | 2.5 | 310 | 0.55 | 8.2 | 295 | 0.85 | 1.6 | 305 | 0.85 | 1.1 | 275 | 0.70 |
| 40 | 3.1 | 310 | 0.50 | 9.4 | 295 | 0.86 | 3.0 | 305 | 0.85 | 1.5 | 275 | 0.72 |
| 50 | 3.3 | 310 | 0.53 | 9.2 | 610, 300 | 0.075. 0.70 | 3.1 | 305 | 0.85 | 1.5 | 275 | 0.72 |
| 60 | 3.2 | 310 | 0.54 | 9.2 | 300 | 0.70 | 3.1 | 305 | 0.85 | 1.6 | 275 | 0.71 |

T = Time of radiation , $\wedge_M$ = molar conductivity *$10^4$ in ohm$^{-1}$ Cm$^2$ mol$^{-1}$ , λ=wave length , A= absorbence

### Table 5 : Radiolytical results of $A_1H$ and $A_2H$ ; formate solution ($N_2$ gas)

| | $A_1H$ Neutral | | | $A_1H$ Basic | | | $A_2H$ Neutral | | | $A_2H$ Basic | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T | $\wedge_M$ | λ (nm) | A | $\wedge_M$ | λ (nm) | A | $\wedge_M$ | λ (nm) | A | $\wedge_M$ | 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<br>270 | 0.51<br>0.60 | 0.70 | 290<br>230 | 0.42<br>0.70 | 1.90 | 280 | 0.60 | 0.70 | 220 | 0.89 |
| 30 | 0.75 | 310<br>270 | 0.50<br>0.60 | 0.65 | 290<br>230 | 0.42<br>0.70 | 0.75 | 280 | 0.62 | 0.50 | 220 | 0.90 |
| 40 | 0.50 | 310<br>270 | 0.50<br>0.60 | 0.40 | 290<br>230 | 0.42<br>0.70 | 0.60 | 280 | 0.62 | 0.40 | 220 | 0.90 |
| 50 | 0.40 | 310<br>270 | 0.50<br>0.60 | 0.30 | 290<br>230 | 0.42<br>0.70 | 0.50 | 280 | 0.62 | 0.20 | 220 | 0.90 |
| 60 | 0.20 | 310<br>270 | 0.50<br>0.60 | 0.20 | 290<br>230 | 0.42<br>0.70 | 0.40 | 280 | 0.62 | 0.20 | 220 | 0.90 |

**Table 6 : Radiolytical results of $A_3H$, $A_4H$ and $A_5H$ ; formate solution ($N_2$ gas)**

| | **$A_3H$ Neutral** | | | **$A_3H$ Basic** | | | **$A_4H$ Neutral** | | | **$A_4H$ Basic** | | | **$A_5H$ Neutral** | | | **$A_5H$ Basic** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T | ^M | λ (nm) | A | ^M | λ (nm) | A | ^M | λ (nm) | A | ^M | λ (nm) | A | ^M | λ (nm) | A | ^ M | λ (nm) | A |
| 0 | 2.50 | 300 | 0.60 | 1.10 | 240 | 0.85 | 2.10 | 270 | 0.8 | 1.7 | 290 | 0.65 | 1.1 | 210 | 0.45 | 1.0 | 230 | 0.3 |
| 5 | 2.50 | 300 | 0.60 | 1.00 | 240 | 0.85 | 2.00 | 270 | 0.8 | 1.5 | 290 | 0.65 | 1.3 | 210 | 0.45 | 1.2 | 230 | 0.3 |
| 10 | 2.30 | 300 | 0.60 | 1.00 | 240 | 0.85 | 2.00 | 270 | 0.8 | 1.2 | 290 | 0.65 | 1.3 | 210 | 0.45 | 1.2 | 230 | 0.3 |
| 15 | 2.50 | 300 | 0.60 | 1.20 | 240 | 0.85 | 1.80 | 270 | 0.8 | 1.2 | 290 | 0.65 | 1.6 | 210 | 0.45 | 1.2 | 230 | 0.3 |
| 20 | 2.40 | 300 | 0.60 | 1.10 | 240 | 0.85 | 1.70 | 270 | 0.8 | 1.0 | 290 | 0.65 | 1.8 | 210 | 0.45 | 1.3 | 230 | 0.3 |
| 30 | 2.40 | 300 | 0.60 | 1.10 | 240 | 0.85 | 1.70 | 270 | 0.8 | 0.9 | 290 | 0.65 | 1.9 | 210 | 0.45 | 1.5 | 230 | 0.3 |
| 40 | 2.50 | 300 | 0.60 | 1.00 | 240 | 0.85 | 1.50 | 270 | 0.8 | 0.6 | 290 | 0.65 | 2.1 | 210 | 0.45 | 1.9 | 230 | 0.3 |
| 50 | 2.50 | 300 | 0.60 | 1.10 | 240 | 0.85 | 1.20 | 270 | 0.8 | 0.4 | 290 | 0.65 | 2.5 | 210 | 0.45 | 2.2 | 230 | 0.3 |
| 60 | 2.50 | 300 | 0.60 | 1.10 | 240 | 0.85 | 1.20 | 270 | 0.8 | 0.2 | 290 | 0.65 | 3.0 | 210 | 0.45 | 2.4 | 230 | 0.3 |

**Table 7 : Radiolytical results of complex 1 -4 ; formate solution ($N_2$ gas)**

| | **Complex 1** | | | **Complex 2** | | | **Complex 3** | | | **Complex 4** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T | ^M | λ (nm) | A | ^M | λ (nm) | A | ^M | λ (nm) | A | ^M | λ (nm) | A |
| 0 | 4.1 | 790, 300 | 0.082, 0.75 | 3.0 | 880, 210 | 0.065, 0.90 | 6.3 | 610, 290 | 0.07, 0.70 | 4.5 | 700, 250 | 0.04, 0.85 |
| 5 | 3.6 | 300 | 0.75 | 2.7 | 880, 210 | 0.064, 0.91 | 5.5 | 290 | 0.71 | 4.1 | 700, 250 | 0.04, 0.83 |
| 10 | 3.3 | 300 | 0.74 | 2.3 | 880, 210 | 0.065, 0.90 | 5.0 | 290 | 0.69 | 3.8 | 700, 250 | 0.04, 0.86 |
| 15 | 2.9 | 300 | 0.74 | 2.0 | 880, 210 | 0.065, 0.92 | 4.3 | 290 | 0.70 | 3.3 | 250 | 0.84 |
| 20 | 2.4 | 300, 345 | 0.75, 0.51 | 1.8 | 210, 320 | 0.95, 0.78 | 3.5 | 290 | 0.70 | 2.8 | 250 | 0.85 |
| 30 | 1.8 | 300, 345 | 0.75, 0.51 | 1.4 | 210, 320 | 0.91, 0.77 | 2.9 | 290 | 0.70 | 2.2 | 250 | 0.85 |
| 40 | 1.2 | 300, 345 | 0.74, 0.52 | 1.1 | 210, 320 | 0.91, 0.78 | 2.4 | 290, 320 | 0.70, 0.58 | 1.9 | 250, 305 | 0.85, 0.91 |
| 50 | 0.8 | 300, 345 | 0.74, 0.52 | 0.6 | 210, 320 | 0.91, 0.78 | 1.8 | 290, 320 | 0.70, 0.56 | 1.4 | 250, 305 | 0.84, 0.90 |
| 60 | 0.3 | 300, 345 | 0.75, 0.51 | 0.2 | 210, 320 | 0.90, 0.78 | 1.2 | 290, 320 | 0.70, 0.58 | 0.6 | 250, 305 | 0.85, 0.90 |

**Table 8 : Radiolytical results of the complexes 5, 6; formate solution ($N_2$ gas)**

| | **Complex 5** | | | | | | **Complex 6** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T | ^M | ^M* | λ (nm) | λ* (nm) | A | A* | ^M | ^M* | λ (nm) | λ* (nm) | A | A* |
| 0 | 2.1 | 2.1 | 700, 220 | 700, 220 | 0.05, 0.91 | 0.05, 0.90 | 0.9 | 0.9 | 640, 210 | 640, 210 | 0.08, 0.70 | 0.08, 0.70 |
| 5 | 2.1 | 2.0 | 700, 220 | 700, 220 | 0.05, 0.91 | 0.05, 0.90 | 0.9 | 0.9 | 640, 210 | 640, 210 | 0.08, 0.70 | 0.08, 0.70 |
| 10 | 2.1 | 2.1 | 700, 220 | 700, 220 | 0.05, 0.91 | 0.05, 0.90 | 1.0 | 0.9 | 640, 210 | 640, 210 | 0.08, 0.70 | 0.08, 0.70 |
| 15 | 2.0 | 2.0 | 700, 220 | 700, 220 | 0.05, 0.91 | 0.05, 0.90 | 0.9 | 0.9 | 640, 210 | 640, 210 | 0.08, 0.70 | 0.08, 0.70 |
| 20 | 2.0 | 2.0 | 700, 220 | 700, 220 | 0.05, 0.91 | 0.05, 0.90 | 1.0 | 0.9 | 640, 210 | 640, 210 | 0.08, 0.70 | 0.08, 0.70 |
| 30 | 2.2 | 2.1 | 700, 220 | 700, 220 | 0.05, 0.91 | 0.05, 0.90 | 0.8 | 0.9 | 640, 210 | 640, 210 | 0.08, 0.70 | 0.08, 0.70 |
| 40 | 2.2 | 2.0 | 700, 220 | 700, 220 | 0.05, 0.90 | 0.05, 0.90 | 0.8 | 0.9 | 640, 210 | 640, 210 | 0.08, 0.70 | 0.08, 0.70 |
| 50 | 2.0 | 2.0 | 700, 220 | 700, 220 | 0.05, 0.90 | 0.05, 0.90 | 1.0 | 0.9 | 640, 210 | 640, 210 | 0.08, 0.70 | 0.08, 0.70 |
| 60 | 2.1 | 2.0 | 700, 220 | 700, 220 | 0.05, 0.90 | 0.05, 0.90 | 1.0 | 0.9 | 640, 210 | 640, 210 | 0.08, 0.70 | 0.08, 0.70 |

- = Data after one hour of irradiation

**Table 9 : Radiolytical results of the complexes 7, 8 ; formate solution ($N_2$ gas)**

| | Complex 7 | | | Complex 8 | | |
|---|---|---|---|---|---|---|
| T | ^M | λ (nm) | A | ^M | λ (nm) | A |
| 0 | 4.6 | 675, 325 | 0.06, 0.77 | 2.0 | 600, 300 | 0.07, 0.60 |
| 5 | 5.0 | 675, 325 | 0.05, 0.76 | 2.3 | 600, 300 | 0.07, 0.60 |
| 10 | 5.4 | 675, 325 | 0.06, 0.76 | 3.0 | 600, 300 | 0.071, 0.60 |
| 15 | 6.1 | 675, 325 | 0.065, 0.78 | 3.4 | 600, 300 | 0.072, 0.62 |
| 20 | 6.8 | 675, 325 | 0.058, 0.77 | 4.0 | 600, 300 | 0.07, 0.61 |
| 30 | 7.5 | 675, 325 | 0.06, 0.79 | 4.5 | 600, 300 | 0.07, 0.60 |
| 40 | 8.1 | 675, 325 | 0.06, 0.77 | 4.9 | 600, 300 | 0.07, 0.60 |
| 50 | 8.8 | 675, 325 | 0.062, 0.77 | 5.2 | 600, 300 | 0.07, 0.61 |
| 60 | 9.3 | 675, 325 | 0.06, 0.77 | 6.0 | 600, 300 | 0.072, 0.61 |

**Table 10 : Radiolytical results of the complexes 9, 10; formate solution ($N_2$ gas)**

| | Complex 9 | | | | | | Complex 10 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $T^*$ | ^M | ^M* | λ (nm) | λ* (nm) | A | A* | ^M | ^M * | λ (nm) | λ* (nm) | A | A* |
| 0 | 2.5 | 2.5 | 700, 250 | 700, 250 | 0.035, 0.80 | 0.035, 0.80 | 1.0 | 1.0 | 790, 290 | 790, 290 | 0.02, 0.62 | 0.02, 0.60 |
| 5 | 3.1 | 3.0 | 700, 250 | 700, 250 | 0.034, 0.80 | 0.035, 0.80 | 1.6 | 1.5 | 790, 290 | 790, 290 | 0.02, 0.62 | 0.02, 0.60 |
| 10 | 3.5 | 3.5 | 700, 250 | 700, 250 | 0.035, 0.81 | 0.035, 0.80 | 2.3 | 2.5 | 790, 290 | 790, 290 | 0.02, 0.61 | 0.02, 0.60 |
| 15 | 4.1 | 4.0 | 700, 250 | 700, 250 | 0.035, 0.80 | 0.035, 0.80 | 3.0 | 3.0 | 790, 290 | 790, 290 | 0.02, 0.60 | 0.02, 0.60 |
| 20 | 4.8 | 4.5 | 700, 250 | 700, 250 | 0.035, 0.81 | 0.035, 0.80 | 3.5 | 3.5 | 790, 290 | 790, 290 | 0.02, 0.60 | 0.02, 0.60 |
| 30 | 5.4 | 4.5 | 700, 250 | 700, 250 | 0.035, 0.82 | 0.035, 0.80 | 3.9 | 4.0 | 790, 290 | 790, 290 | 0.02, 0.61 | 0.02, 0.60 |
| 40 | 6.2 | 6.0 | 700, 250 | 700, 250 | 0.035, 0.80 | 0.035, 0.80 | 4.5 | 4.5 | 790, 290 | 790, 290 | 0.02, 0.60 | 0.02, 0.60 |
| 50 | 7.1 | 7.0 | 700, 250 | 700, 250 | 0.035, 0.80 | 0.035, 0.80 | 5.2 | 5.2 | 790, 290 | 790, 290 | 0.02, 0.60 | 0.02, 0.60 |
| 60 | 8.0 | 8.0 | 700, 250 | 700, 250 | 0.035, 0.80 | 0.035, 0.80 | 6.5 | 6.5 | 790, 290 | 790, 290 | 0.02, 0.60 | 0.02, 0.60 |

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