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Radiolysis of Cobalt (II) and Nickel (II) – Complexes Containing Mixed Ligands by Gamma Rays

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Abstract

The effect of gamma-radiation has been studied directly on some solid complexes cobalt (II) and nickel (II) complexes having the formula $[M_2(LH_2)_2(AH_2)_2(NO_3)_2](NO_3)_2$, $[M_2(LH_2)_2(AH_2)_2X_n]$ and $[M_2(SCH)_2(AH)_2]$ (where M = Co^{+2} or Ni^{+2}, AH_2 = any of the following carboxylic acid " salicylic acid–SH_2 , anthranilic acid–AnH_2 or phthalic acid–PH_2", LH_2=salicylaldehyde semicarbazone–SCH_2 or salicylaldehyde thiosemicarbazone-STH_2 , X= CO_3^{-2} or $CH_3CO_2^{-}$; n = 0, 2 or 4). Ionization and excitation of these complexes have been achieved . The melting or decomposition points, conductivities and electronic spectral data have been indeed related to the final stable products . The results showed that some of the complexes have been decomposed by gamma ray, others complexes have not been affected . Very interesting results have been obtained in the case of, $[Co_2(SH_2)_2(SCH_2)_2(NO_3)_2](NO_3)_2$, $[Ni_2(SH_2)_2(STH_2)_2(NO_3)_2](NO_3)_2$, $[Co_2(SH)_2(SCH)_2]$, $[Ni_2(AnH_2)_2(STH_2)_2(NO_3)_2](NO_3)_2$, $[Ni_2(PH_2)_2(STH_2)_2(NO_3)_2](NO_3)_2$, $[Co_2(PH)_2(SCH)_2]$ in which a sort of polymerization have been exhibited after their radiolysis .

الخلاصة

يتضمن دراسة تأثير أشعة كاما على بعض المعقدات الصلبة مباشرة للكوبلت (II) والنيكل (II) الحاوية على مزيج من الليكاندات سالسالديهايدسميكاربازون- SCH_2 أو سالسالديهايدثايوسميكاربازون - STH_2 والأحماض الكاربوكسيلية (حامض السالساليك - SH_2 أو الانثرانيليك- AnH_2 أو الفثاليك - PH_2) ذات الصيغ $[M_2(LH_2)_2(AH_2)_2X_n]$ و$[M_2(LH_2)_2(AH_2)_2(NO_3)_2](NO_3)_2$ و$[M_2(SCH)_2(AH)_2]$ (حيث M=Co^{+2} أوNi^{+2} و AH_2 = أحدالأحماض الكاربوكسيلية أعلاه و LH_2 = سالسالديهايد سميكاربازون أو سالسالديهايدثايو سميكاربازون و X = CO_3^{-2} أو $CH_3CO_2^{-}$ و n = صفر أو 2 أو 4) ، حيث ينتج تأين واثارة لهذه المعقدات . تعود درجات الانصهار أو التفكك والتوصيلية وطيف الأشعة فوق البنفسجية الى المركبات المستقرة النهائية . أوضحت النتائج أن بعض المعقدات تتفكك بفعل أشعة كاما وبعضها الاخر يحدث لها بلمرة كالمعقدات ذات الصيغ : $[Co_2(SH_2)_2(SCH_2)_2(NO_3)_2](NO_3)_2$ و $[Ni_2(SH_2)_2(STH_2)_2(NO_3)_2](NO_3)_2$ و $[Co_2(SH)_2(SCH)_2]$ و $[Ni_2(AnH_2)_2(STH_2)_2(NO_3)_2](NO_3)_2$ و $[Ni_2(PH_2)_2(STH_2)_2(NO_3)_2](NO_3)_2$ و $[Co_2(PH)_2(SCH)_2]$ وهي نقطة مهمة لما للبوليمرات من اهمية حاليا .

Introduction

The effect of any ionizing radiation started with an interaction between radiation and the molecules . There have been two different types of interactions either direct effect which observed in the same molecule where the primery absorption occurred or indirect effect in which the radiation energy has been absorbed in another molecule (solvent) resulting in the formation of reactive products that subsequently reacted with other molecules in the system . In a dry system (without solvent) , only the direct effect occurred(1) .

A good deal of work has been reported on the radiolysis of complexes in solutions , this is due to the capability of the active species (.OH, H$^{.}$,e$^{-}_{aq}$, …….. …..etc) of affecting on metal-complexes(2) . A large body of radiolysis of metal-complexes in solutions have been reported(2-5) .

The direct gamma irradiation effects (without solvent)have been studied widely on some organic, biological and amorphous compounds(6-10), whereas on the solid metal-complexes a few articles were reported(11-21)

It was well-known that the reaction of the ligand molecule in coordination compounds have been affected by the central metal ions .The direct excitation of the complexes by an ionizing radiation can be expected in the radiolysis of crystalline complexes(11) .The study on the radiolysis of crystalline metal complexes was also considered to be very helpful for the elucidation of the mechanism of the reaction affected by metal ions(12) . The anion (eg. $C_2O_4^{-2}$) in metal salt (eg. $Na_2C_2O_4$) was very stable to gamma ray irradiation , compared with those in metal-ligand (as metal oxalato) complexes . The fairly large reactivity of the complexes toward gamma irradiation may be attributed to the covalent character of ligand-metal bond . The ligand ions with large covalent character decomposed more easily by gamma irradiation(11,13) . The oxalato complexes were irradiated with gamma rays at room temperature(11,14,15) . The much larger G values of Fe^{2+} and Co^{2+} complexes than that of Al^{3+} complex can not be explained only by the covalent character of the ligand-metal bond , but they seemed to be related with the reduction of metal ions . On gamma irradiation of Fe^{3+} and Co^{3+} complex , the reduction of the metal ions also occurred , and ferrous and cobaltous oxalate participitated when the irradiated complexes were dissolved in water . Therefore, the electron transfer from the ligand (oxalate) to metal ion might increase the radiation-induced decomposition of the ligand (oxalate) . While in the case of gamma irradiation of chromium complex , the electron transfer from ligand (oxalate) to metal ion might be difficult and this might cause the lower G value of Cr^{3+} complex than those of Fe^{3+} and Co^{3+} complexes . But on the reaction of Cr^{3+} complex the oxidation of Cr^{3+} to Cr^{6+} might occur, and a fairly large amount of CO was formed inplace of CO_2 which was main product in the gamma irradiation of the oxalate complexes other than those with Cr^{3+} (15) .

A protective effect of certain metal ions on the enzymatic activity of gamma irradiated dry trypsin was first discovered(16) . Subsequently, several studies on the effects of metal ions in decreasing the initial radical yields in various proteins, nucleic acid and related substances(16-20) were carried out . Complexes were consistent with the hypothesis that cupric ions were acting as electron scavengers(19) . The effect of copper (II), iron (II), nickel (II) and cadmium (II) ions on the gamma radiolysis of collagen and polyadenylic acid in the solid state were also investigated in the absence of air(21) . The effect of metal ions were found in reducing the radiation-induced , decreasing of the average molecular weight and the formation of stable carbon radicals at room temperature(21) . There was a considerable degree of similarity between the effects of ions in preventing the radiation induced formation of carbon radicals and the decrease of average molecular weight in collagen and polyadenylic acid . For the

DNA-metal complexes, we have observed that metal ions decreased the initial radical yield at 77 ^{0}K and at 298 ^{0}K to approximately the same extent(18) . The effect of gamma radiation has been studied directly on the solid Schiff base-complexes of copper (II), cobalt (II) and nickel (II) resulting in ionization and excitation of these complexes . Gamma-irradiation caused the decomposition of some complexes and polymerization in the other complexes(12,22)

The one-electron reduction of several metal bis-dithiolenes at the surface of TiO_2 particles have been studied using variable temperature EPR measurements following band-gap excitation of the particles showed the disappearance of signals due to paramagnetic Ni (III) and Cu (II) complexes of 4,5-dimercuptophthalic acid, 3,4-dimercuptotoluene and malconitrile dithiolate with the surface electron signals vanishing concomitantly . Similarly , the diamagnetic Cu (II) complex of 3,4- dimercaptotoluene was reduced to paramagnetic Cu (II) complexes(23) . The triplet state has been studied for solid complexes(24) .

To the best of available knowledge , the effect of gamma irradiation on some mixed ligand (semicarbazone and substituted carboxylic acid) complexes of cobalt (II) and nickel (II), have not yet been reported . It is a matter of interest to determine the extent to which gamma irradiation for these complexes would be affected .

Experimental

1. **Preparation of the compounds :**

The ligands salicylaldehyde semicarbazone(25-27) and salicylaldehyde thiosemicarba- zone(26,28-31) have been prepared according to the literature methods . The complexes in neutral and basic medium have been synthesised according to the previous methods (26-31) .

2. **Radiolysis of the complexes :**

All gamma irradiation have been carried out using gamma cell-220 purchased from the Canadian Atomic Energy . The solid complexes were put in a fine cylindrical tubes and the tubes were sealed . Irradiation of the complexes have been carried out in different interval times (5, 10, 15, 20, 30, 40, 50 and 60 minutes) under 4.52×10^{16} ev. ml^{-1}. Min^{-1} dose rate . The complexes before and after irradiation were dissolved in dimethyl- formamide (for comparison) in order to measure their absorbance and conductivities .

3. **Conductivity and spectral measurements :**

Molar conductivities of the complexes (before and after irradiation) have been measured in an electrolytic conductivity measuring set LF-42 and Multiline F/SET-2 WTW using 10^{-3} M dimethylformamide at room temperature .

The electronic spectra of the complexes (before and after gamma-irradiation) in 10^{-4} M dimethylformamide solutions, have been recorded on Shimadzu UV-Visible Recording Spectrophotometer -160 and Shimadzu Double-beam Spectrophotometer UV-210A .

Results & Discussion

The radiolysis of solid matter caused ionization , ejection of electrons from some atoms and exitation accompained by chemical reactions and decomposition .

$[ML_n]$ ~~~→ $[ML_n]^*$, $[ML_{n-y}]^+ + {}_yL^-$, e

(complex) (exited molecule) (ions) (ejected electron)

The effect of the coordinated ligands in the complexes was more reactive under ionization radiation , i.e. the covalency between the ligand and metal was important for the reactivity of the ligands against ionizing radiation than the free ligand . In addition to the effect of covalency , the oxidation and reduction of the central metal ions affected the reaction mechanism of the ligand . Gamma-irradiation brought about the decomposition of the ligand, breakage of hydrogen bonding and a change in the oxidation state of metal ions , the decomposition could be completely giving gaseous liquid and solid products(11-14, 22, 27) .

The effect of ionizing radiation on some complexes containing mixed ligand in solid state have been carried out by exposing these complexes to gamma radiation in different time intervals ranging between 5-60 minutes . The changes which happened in these complexes have been noticed by following the changes in melting or decomposition points , the changes in electronic spectra and the changes of molar conductivity before and after the exposure to ionizing radiation . Different effects for these complexes have been happened (Tables 1-10), some complexes have been resistant to radiation and others showed partial changes, while the other complexes showed noticed changes. The melting points of the complexes were measured directly after gamma irradiation, the changes observed were as follows :

complexes 1, 2, 7, 13, 17, 18, 20 and 24 showed changes in the melting or decomposition points and a decrease in the molar conductivities values in addition to the appearance of another band in the electronic spectra of theinvestigated irradiated complexes, these changes may indicate the formation of oligomerersor polymers which considered indeed as a very interesting result . The reaction mechanism proposed for these complexes may be represented by the following reaction :

$[M_2(L)_2(S)_2X_n] \sim\longrightarrow [M_2(L)_2(S)_2X_n]^{\cdot}$

$[M_2(L)_2(S)_2X_n]^{\cdot} + [M_2(L)_2(S)_2X_n] \sim\longrightarrow \{[M_2(L)_2(S)_2X_n]_2\}^{\cdot}$

$\}[M_2(L)_2(S)_2X_n]_2\}^{\cdot} + [M_2(L)_2(S)_2X_n] \sim\longrightarrow \{[M_2(L)_2(S)_2X_n]_3\}^{\cdot}$

The polymerization process continued and the final product resulted is having the formula $[M_2(L)_2(S)_2X_n]_m$ (where M= the metal ion Co^{+2} or Ni^{+2} , L= the carboxylic acid ligands , S= semicarbazone or thiosemicarbazone ligand , X= the counter ion in the investi- gated complexes , n= number of the counter ion , m= number of the complex molecules)

Complexes 3, 14, 15, 16, 23 and 25 showed changes in the melting or decomposition points and a decrease in molar conductivities values but no addition bands in the electronic spectra appeared . These changes may be due to attachment of the counter ion by radiolysis which lead to the formation of oligomer or polymer . The proposed reaction mechanism may be represented by the following reactions :

$[M_2(L)_2(S)_2(NO_3)_2](NO_3)_2 \sim\longrightarrow \{[M_2(L)_2(S)_2(NO_3)_2](NO_3)_2\}^*$

$\{[M_2(L)_2(S)_2(NO_3)_2](NO_3)_2\}^* \sim\longrightarrow \{[M_2(L)_2(S)_2(NO_3)_2]NO_3\}^{1+*} + NO_3^{\cdot -}$

$\{[M_2(L)_2(S)_2(NO_3)_2]NO_3\}^{1+*} \sim\longrightarrow [M_2(L)_2(S)_2(NO_3)_2]^{2+*} + NO_3^{\cdot -}$

$\{[M_2(L)_2(S)_2(NO_3)_2]\}^{2+*} + [M_2(L)_2(S)_2(NO_3)_2](NO_3)_2 \sim\longrightarrow [M_2(L)_2(S)_2(NO_3)_2]^{2+} + [M_2(L)_2(S)_2(NO_3)_2]^{\cdot} + NO_3^{\cdot -\cdot}$

$[M_2(L)_2(S)_2(NO_3)_2]^{,} + [M_2(L)_2(S)_2(NO_3)_2]^{\cdot} \sim\longrightarrow [M_2(L)_2(S)_2(NO_3)_2]_m$

$[M_2(L)_2(S)_2(NO_3)_2](NO_3)_2 + [M_2(L)_2(S)_2(NO_3)_2]^{2+} \sim\longrightarrow \{[M_2(L)_2(S)_2(NO_3)_2]^{2+}\}_m + 2NO_3^{>-}$

$6NO_3^{\cdot -} \rightarrow 6NO_2 + 3O_2$

Complexes 4, 6, 9, 11 and 22 showed a decrease in the melting or decomposition points and an increase in the molar conductivities values in addition to the appearance of new band in the electronic spectra of the irradiated complexes . The proposed reaction mechanism may be represented as follows:

$[M_2(L)_2(S)_2X_n] \sim\longrightarrow [M_2(L)_2(S)_2X_{n-1}]^{\cdot +*} + X^{\cdot -}$

$[M_2(L)_2(S)_2X_{n-1}]^{\cdot +*} \sim\longrightarrow \{[M_2(L)_2(S)_2X_{n-2}]^{2+*} + X^{\cdot -}$

$[M_2(L)_2(S)_2X_{n-2}]^{2+*} + 2X^{\cdot -} \rightarrow \{[M_2(L)_2(S)_2X_{n-2}]^{\cdot}X_2$

Complexes 10, 12, 19, 27, 28 and 29 showed an increase in the melting or decomposition points and an increase in the molar conductivities values in addition to the appearance of new band in the electronic spectra of the irradiated complexes, this may be due to the decomposition of the dimeric complexes and either changed to monomer or completely decomposed . The proposed reaction mechanism may be represented as follows:

$[M_2(L)_2(S)_2X_n] \sim\!\longrightarrow [M_2(L)_2(S)_2]^{n+*} + nX^{\cdot -}$

$[M_2(L)_2(S)_2X_n] + [M_2(L)_2(S)_2]^{n+*} \sim\!\longrightarrow [M_2(L)_2(S)_2]^{n+} + [M_2(L)_2(S)_2]^{\cdot}$

$[M_2(L)_2(S)_2]^{\cdot} \sim\!\longrightarrow 2[M(L)(S)]$

$2[M(L)(S)]^{n+*} + nX^{\cdot -} \dashrightarrow 2[M(L)(S)]X$

Complexes 26 showed change in the melting or decomposition points and an increase in the molar conductivities values and changes in the absorbance but no band appeared in the electronic spectra of the irradiated complex, this may be due to the breakage of the hydrogen bonding and changes in the structure of the complexes.

Complexes 5 and 21 did not show any changes in the melting or decomposition points but showed an increase in the molar conductivities values in addition to the appearance of new band in the electronic spectra of the irradiated complexes, this may be due to the breakage of the hydrogen bonding . The proposed reaction mechanism may be represented as follows:

$[M_2(L)_2(S)_2X_n] \sim\!\longrightarrow [M_2(L)_2(S)_2X_{n-1}]^{\cdot 1+*} + X^{\cdot -}$

$[M_2(L)_2(S)_2X_n] + [M_2(L)_2(S)_2X_{n-1}]^{1+*} \sim\!\longrightarrow \{[M_2(L)_2(S)_2X_{n-2}]^{2+*\cdot} + X^{\cdot -}$

$[M_2(L)_2(S)_2X_{n-2}]^{+2} + 2X^{\cdot -} \longrightarrow \{[M_2(L)_2(S)_2X_z]^{\cdot}X_2$

Table – 1 : Results of radiolysis for cobalt complexes prepared in neutral medium

T*	$1^{(26,30)}$ $[Co_2(SH_2)_2(SCH_2)_2(NO_3)_2](NO_3)_2$				$2^{(26,30)}$ $[Co_2(AnH_2)_2(SCH_2)_2(NO_3)_2](NO_3)_2$				$3^{(26,30)}$ $[Co_2(PH_2)_2(SCH_2)_2(NO_3)_2](NO_3)_2$			
	M.P. ^0C	^M **	λ ***	A ****	M.P. ^0C	^M **	λ ***	A ****	M.P. ^0C	^M **	λ ***	A ****
0	117	103	395	1.686	180	73	385	1.610	150	136	380	1.483
5	114	32	395	1.616	196	35	385 391	1.086 1.548	149	21	380	0.864
10	114	36	395	1.614	192	38	385 391	1.065 1.564	135	15	380	1.495
15	119	40	395 377	0.958 1.246	180	40	385 395	1.174 1.570	125	5	380	0.848
20	129	35	395 374	0.942 1.253	174	50	385 391	1.182 1.547	120	6	380	0.649
30	126	38	395 380	1.333 1.497	178	45	385 392	1.035 1.276	118	5	380	1.136
40	124	45	395 383	1.470 1.553	185	52	385 391	1.103 1.586	114	2	380	0.959
50	130	52	395 390	1.520 1.594	182	32	385 391	1.147 1.590	112	15	380	1.215
60	140	56	395 388	1.556 1.582	176	30	385 391	1.032 1.583	112	20	380	1.649

M.P. : Melting points or decomposition points

* T : Time of irradiation

** ^M : Molar conductivities in $\Omega^{-1}\,cm^2\,mol^{-1}$

*** λ : Wave lengh in nanometer

**** A : Absorbance

Table – 2 : Results of radiolysis for cobalt complexes prepared in neutral medium

T*	4[26,30] $[Co_2(SH_2)_2(SCH_2)_2(Ac)_4$				5[26,30] $[Co_2(AnH_2)_2(SCH_2)_2(Ac)_4]$				6[26,30] $[Co_2(PH_2)_2(SCH_2)_2(Ac)_4]$			
	M.P. ^{0}C	^M **	λ ***	A ****	M.P. ^{0}C	^M **	λ ***	A ****	M.P. ^{0}C	^M **	λ ***	A ****
0	284	11	409	1.661	286	16	416	1.640	270	0	408	1.643
5	n.m	32	409 395	1.346 1.590	286	30	416 402	1.113 1.614	180	2	408 390	1.096 1.583
10	n.m	38	409 395	1.385 1.604	286	28	416 402	1.143 1.605	160	12	408 393	1.191 1.595
15	260	54	409 395	1.385 1.595	286	24	416 398	0.908 1.565	180	3	408 387	0.840 1.547
20	260	51	409 395	1.418 1.593	286	32	416 398	0.793 1.546	120	0	408 393	1.184 1.594
30	260	44	409 395	1.171 1.352	286	29	416 398	0.785 1.549	120	10	408 390	1.050 1.579
40	260	90	409 395	1.285 1.572	286	22	416 400	0.990 1.568	120	14	408 398	1.102 1.588
50	260	41	409 395	1.447 1.603	286	20	416 397	0.843 1.556	140	14	408 390	1.022 1.578
60	260	63	409 395	1.630 1.622	286	25	416 397	0.703 1.523	144	15	408 390	1.007 1.580

n.m. = not melt or decomposed at 265 ^{0}C

Table – 3 : Results of radiolysis for cobalt complexes prepared in neutral medium

T*	7[26,30] $[Co_2(SH_2)_2(SCH_2)_2(CO_3)_2]$				8[26,30] $[Co_2(AnH_2)_2(SCH_2)_2(CO_3)_2]$				9[26,30] $[Co_2(PH_2)_2(SCH_2)_2(CO_3)_2]$			
	M.P ^{0}C	^M **	λ ***	A ****	M.P. ^{0}C	^M **	λ ***	A ****	M.P. ^{0}C	^M **	λ ***	A ****
0	275	26	408	1.656	270	28	410	1.638	210	0	407	1.646
5	n.m	7	408 380	0.779 1.299	n.m	35	410	1.638	210	40	407 373	0.573 1.374
10	n.m	8	408 380	1.779 1.299	265	36	410	1.638	200	55	407 366	0.346 1.063
15	260	11	408 393	1.205 1.555	262	38	410	1.638	195	65	407 363	0.458 1.315
20	260	13	408 390	1.039 1.499	260	32	410	1.638	195	70	407 364	0.463 1.193
30	260	13	408 380	0.644 1.184	295	35	410	1.638	190	68	407 371	0.361 1.111
40	258	15	408 387	1.543 1.543	264	25	410	1.638	185	70	407 363	0.490 1.241
50	258	15	408 390	1.219 1.574	268	30	410	1.638	178	61	407 371	0.533 1.320
60	258	20	408 383	0.963 1.510	254	38	410	1.638	170	68	407 372	0.439 1.248

Table – 4 : Results of radiolysis for cobalt complexes prepared in basic medium

T*	10[26,30] $[Co_2(SH)_2(SCH)_2]$				11[26,30] $[Co_2(AnH)_2(SCH)_2]$				12[26,30] $[Co_2(PH)_2(SCH)_2]$			
	M.P ^{0}C	^M **	λ ***	A ****	M.P. ^{0}C	^M **	λ ***	A ****	M.P. ^{0}C	^M **	λ ***	A ****
0	238	12	407	1.630	280	0	407	1.641	245	0	415	1.642
5	235	22	407 385	1.132 1.575	n.m	0	407 392	1.370 1.610	260	10	415 391	1.271 1.612
10	230	22	407 385	1.206 1.079	n.m	0	407 394	1.394 1.691	260	5	415 394	1.394 1.621
15	230	15	407 385	1.419 1.600	265	5	407 392	1.453 1.623	240	5	415 388	1.108 1.592
20	250	12	407 385	1.439 1.604	265	12	407 394	1.423 1.612	235	8	415 395	1.502 1.628
30	260	28	407 385	1.543 1.626	265	15	407 394	1.502 1.628	230	8	415 394	1.451 1.622
40	262	14	407 385	1.557 1.624	265	10	407 392	1.529 1.637	228	0	415 393	1.291 1.612
50	260	10	407 385	1.179 1.540	265	6	407 394	1.451 1.620	250	14	415 397	1.423 1.621
60	260	10	407 385	1.392 1.603	245	10	407 394	1.390 1.621	260	5	415 403	1.620 1.637

Table – 5 : Results of radiolysis for cobalt complexes prepared in neutral medium

T*	13[26,31] $[Co_2(SH_2)_2(STH_2)_2(NO_3)_2](NO_3)_2$				14[26,31] $[Co_2(AnH_2)_2(STH_2)_2(NO_3)_2](NO_3)_2$				15[26,31] $[Co_2(PH_2)_2(STH_2)_2(NO_3)_2](NO_3)_2$			
	M.P. ^{0}C	^M **	λ ***	A ****	M.P. ^{0}C	^M **	λ ***	A ****	M.P. ^{0}C	^M **	λ ***	A ****
0	176	122	422	1.670	175	132	425	1.665	200	122	426	1.639
5	200	44	422 424	0.921 1.220	180	50	425	1.598	200	52	426	1.633
10	210	55	422 428	1.446 1.624	190	50	425	1.615	215	55	426	1.639
15	225	65	422 428	1.386 1.626	190	50	425	1.611	220	50	426	1.639
20	230	70	422 428	1.467 1.631	200	61	425	1.626	220	56	426	1.644
30	230	68	422 428	1.397 1.634	180	65	425	1.614	220	53	426	1.639
40	230	74	422 428	1.455 1.636	170	55	425	1.612	220	58	426	1.641
50	230	61	422 428	1.215 1.634	170	50	425	1.614	220	46	426	1.639
60	230	68	422 428	1.414 1.639	170	65	425	1.614	220	64	426	1.644

Table – 6A : Results of radiolysis for nickel complexes prepared in neutral medium

T*	16[26] $[Ni_2(SH_2)_2(SCH_2)_2(NO_3)_2](NO_3)_2$				17[26] $[Ni_2(AnH_2)_2(SCH_2)_2(NO_3)_2](NO_3)_2$			
	M.P. ^0C	$\wedge_M$ **	λ ***	A ****	M.P. ^0C	$\wedge_M$ **	λ ***	A ****
0	150	161	395	1.617	180	129	398	1.627
5	80	50	395	1.609	160	31	398 380	1.302 1.502
10	160	35	395	1.394	145	50	398 380	1.573 1.597
15	110	45	395	1.240	140	35	398	1.641
20	146	35	395	1.444	138	35	398	1.623
30	130	40	395	1.325	130	45	398	1.617
40	120	45	395	1.526	128	61	398	1.647
50	120	54	395	1.607	142	52	398	1.621
60	110	45	395	1.626	132	65	398	1.607

Table – 6B : Results of radiolysis for nickel complexes prepared in neutral medium

T*	18[26] $[Ni_2(SH_2)_2(SCH_2)_2(Ac)_4]$				19[26] $[Ni_2(AnH_2)_2(SCH_2)_2(Ac)_4]$			
	M.P. ^0C	$\wedge_M$ **	λ ***	A ****	M.P. ^0C	$\wedge_M$ **	λ ***	A ****
0	245	30	391	1.622	290	5	400	1.630
5	260	6	391 398	0.913 1.033	n.m	20	400 384	1.412 1.622
10	260	2	322	1.592	n.m	21	400	1.916
15	260	3	391 382	1.516 1.592	n.m	29	400	1.594
20	260	0	391 382	1.542 1.592	n.m	23	400 381	1.418 1.572
30	260	5	391 382	2.472 1.582	n.m	12	400 379	1.065 1.413
40	260	5	391 382	1.502 1.582	n.m	17	400 374	0.970 1.371
50	260	0	391 382	1.580 1.580	n.m	18	400 383	1.465 1.577
60	260	0	391 382	1.541 1.592	n.m	24	400 366	0.948 1.321

Table – 7 : Results of radiolysis for nickel complexes prepared in neutral medium

T*	20(26) $[Ni_2(SH_2)_2(SCH_2)_2(CO_3)_2]$				21(26) $[Ni_2(AnH_2)_2(SCH_2)_2(CO_3)_2]$				22(26) $[Ni_2(PH_2)_2(SCH_2)_2(CO_3)_2]$			
	M.P ^{0}C	^M **	λ ***	A ****	M.P. ^{0}C	^M **	λ ***	A ****	M.P. ^{0}C	^M **	λ ***	A ****
0	270	27	390	1.616	n.m	5	407	1.646	290	16	402	1.634
5	260	17	390	1.025	n.m	25	407 390	0.863 1.302	260	20	402	1.586
10	256	17	390	0.877	n.m	18	407 390	0.282 0.495	260	28	402 400	1.527 1.603
15	254	16	390	0.927	n.m	30	407 395	1.203 1.501	255	52	402 400	1.578 1.589
20	252	17	390	1.074	n.m	28	407 395	1.124 1.460	250	40	402 400	1.590 1.615
30	244	17	390	1.075	n.m	26	407 395	1.201 1.503	246	42	402 400	1.592 1.615
40	240	15	390 354	0.185 1.023	n.m	31	407 395	1.266 1.515	240	30	402 408	1.581 1.680
50	240	25	390	1.185	n.m	30	407 395	1.353 1.553	238	32	402 408	1.586 1.603
60	240	16	390 354	0.134 0.958	n.m	30	407 390	0.614 1.007	235	34	402 400	1.580 1.601

Table – 8 : Results of radiolysis for nickel complexes prepared in neutral medium

T*	23(26,27) $[Ni_2(SH_2)_2(STH_2)_2(NO_3)_2](NO_3)_2$				24(26,27) $[Ni_2(AnH_2)_2(STH_2)_2(NO_3)_2](NO_3)_2$				25(26,27) $[Ni_2(PH_2)_2(STH_2)_2(NO_3)_2](NO_3)_2$			
	M.P. ^{0}C	^M **	λ ***	A ****	M.P. ^{0}C	^M **	λ ***	A ****	M.P. ^{0}C	^M **	λ ***	A ****
0	165	120	409	1.648	143	130	425	1.661	185	160	413	1.644
5	165	38	409	1.644	140	63	425 379	1.392 1.584	184	48	413	1.206
10	165	38	409	1.643	150	63	425 374	0.980 1.505	184	50	413	1.284
15	162	30	409	1.641	150	65	425 375	1.024 1.540	190	35	413	0.943
20	170	32	409	1.643	170	60	425 374	1.002 1.531	190	47	413	1.642
30	168	40	409	1.639	150	63	425 377	1.112 1.555	190	48	413	1.540
40	160	39	409	1.636	150	68	425 374	1.980 1.520	190	50	413	1.232
50	156	34	409	1.631	150	67	425 375	1.144 1.565	190	54	413	1.408
60	156	31	409	1.630	150	69	425 374	1.196 1.552	190	58	413	1.204

Table – 9 : Results of radiolysis for nickel complexes prepared in neutral medium

T*	26(26,27) $[Ni_2(SH_2)_2(STH_2)_2(CO_3)_2]$				27(26,27) $[Ni_2(AnH_2)_2(STH_2)_2(CO_3)_2]$				28(26,27) $[Ni_2(PH_2)_2(STH_2)_2(CO_3)_2]$			
	M.P ^0C	^M **	λ ***	A ****	M.P. ^0C	^M **	λ ***	A ****	M.P. ^0C	^M **	λ ***	A ****
0	260	11	425	1.648	264	24	425	1.629	n.m	24	425	1.621
5	260	36	425	1.644	n.m	51	425 367	0.953 1.538	n.m	48	425 370	0.873 1.374
10	245	30	425	1.643	260	34	425 367	0.861 1.430	265	55	425 370	0.921 1.446
15	258	10	425	1.641	256	14	425 367	0.792 1.400	260	44	425 370	0.975 1.371
20	236	8	425	1.643	260	25	425 367	0.714 1.375	254	38	425 370	0.948 1.412
30	258	20	425	1.639	262	20	425 367	0.686 1.453	256	23	425 374	1.230 1.572
40	260	47	425	1.636	n.m	29	425 367	0.784 1.461	236	11	425 370	1.065 1.413
50	260	54	425	1.631	n.m	30	425 367	0.813 1.483	264	50	425 370	1.371 1,521
60	260	50	425	1.630	240	35	425 367	0.844 1.517	264	52	425 370	0.938 1.577

Table – 10 : Results of radiolysis for nickel complexes prepared in basic medium

T*	29(26,27) $[Ni_2(SH)_2(STH)_2]$				30(26,27) $[Ni_2(AnH)_2(STH)_2]$				31(26,27) $[Ni_2(PH)_2(STH)_2]$			
	M.P ^0C	^M **	λ ***	A ****	M.P. ^0C	^M **	λ ***	A ****	M.P. ^0C	^M **	λ ***	A ****
0	290	10	422	1.646	n.m	17	423	1.660	n.m	10	415	1.665
5	n.m	30	422 424	1.357 1.584	n.m	16	423	1.647	n.m	15	415	1.652
10	n.m	30	422 424	1.357 1.584	n.m	12	423	1.648	n.m	13	415	1.652
15	n.m	30	422 424	1.262 1.579	n.m	15	423	1.640	n.m	18	415	1.654
20	n.m	28	422 426	1.240 1.590	n.m	12	423	1.648	n.m	15	415	1.652
30	n.m	29	422 424	1.183 1.466	n.m	14	423	1.655	n.m	14	415	1.654
40	n.m	20	422 424	1.185 1.523	n.m	17	423	1.654	n.m	16	415	1.653
50	n.m	25	422 426	1.095 1.556	n.m	10	423	1.653	n.m	13	415	1.653
60	n.m	22	422 428	1.094 1.563	n.m	14	423	1.647	n.m	17	415	1.653

Complexes 8, 30 and 31 did not show noticable changes with increasing the time of irradiation, this is a very good point and having benefit since these complexes resist the radiation and not affected by ionizing radiation .

According to the observed results . We could propose the following(32-34) : In the complexes that resist gamma rays , we suggest the occurance of ion pair formation leadind to back reaction between emitted electrons and positive ions. In the compound containing electron with drawing groups(32) on aromatic phenyl ring , we could notice that these groups could decrease the stability of the positive ions formed by gamma ray, i.e., increasing their activities towards neutralization with the trapped electrons in the molecules in solid state . Therefore a kind of repairing and removal of gamma-irradiation effects may have happened in the complexes containing electron with drawing groups . In the complexes containing electron donating groups , in addition to the changes in the intensity of electronic spectra , there have been also changes in molar conductivities and melting points . The increase in molar conductivities refers to the increase in decomposition of the complexes while the decrease in molar conductivity may be attributed to recombination of ionization products giving rise to dimers, oligomers or polymers(32-34) .

Conclusion

From the above studies we could conclude three types of effects :

1- Some complexes have been decomposed giving either monomers or may have been decomposed completely by gamma-irradiation .

2- Other complexes were resistant to the ionizing radiation of gamma-rays due to back reaction between positive ions and emitted electrons .

3-Other complexes polymerized by gamma-irradiation .

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