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FURTHER STUDIES ON THE EFFECTS OF TEMPERATURE AND γ-RADIATION DOSES ON THE ELECTRICAL CONDUCTIVITY OF SOLID METAL COMPLEXES

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ABSTRACT

The prepared dry solid metal complexes were compressed at a saturated and suitable pressure of 400 kg cm^{-2} at room temperature into pellets 1.22 cm in diameter and 0.2 cm thick. The DC electrical conductivity was measured at room and elevated temperatures up to 388 K. The test samples were then subjected to various γ-radiation doses ranging from 10^7 to 10^{10} rads, using a ^{60}Co gamma cell. The temperature dependence of electrical conductivity was also undertaken before and after each radiation dose.

The results obtained indicate that the materials under investigation exhibit semiconducting properties in the temperature range studied. The dependence of electrical conductivity and activation energy on temperature and γ-radiation doses is discussed and correlated with the type of substitution and the polymeric nature of the complex. The relative stability of the investigated materials towards irradiation damage is established and discussed on the bases of the ligand field strength and γ-irradiation induced polymerization.

INTRODUCTION

The current interest [1,2] in electron transport phenomena in organic molecular crystals, charge transfer complexes, coordination compounds and radical anion salts prompted this report of the results of a study concerning electrical conduction properties as a function of temperature and γ-irradiation of recently discovered transition metal chelates.

Rosa and Schrauzer [3] deduced that the transition metal chelates of ligands derived from γ-dithioketones exhibit semiconducting behaviour comparable with large organic aromatic hydrocarbons and charge transfer complexes. Polymeric and nonpolymeric complexes of 5-ethyl pyrimidine, with copper(I), copper(II) and silver(I) were prepared and investigated [4], showing a high electrical conductivity for the polymeric ones. The prepared iron(II), copper(II), cobalt(II), nickel(II) and zinc(II) dinitrosoresorcinol

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complexes [5] were found to possess semiconducting properties in the temperature range 20—115° C. For bis-copper, cobalt, nickel and zinc complexes, the conductivity increased and the activation energy decreased.

Radiation of long chain [6] molecules resulted in either crosslinkage or reduction of molecular weight by fracture of chain, or both. The crosslinkage produced in polyethylene alters its physical properties [6]. Sharn [7] investigated the radiation damage of organic solids exposed to ^{60}Co X-rays. Elagramy et al. [8] studied the induced electrical conductivity of γ-irradiated 8-hydroxyquinoline metal complexes showing a decrease in the electrical conductivity and an increase in activation energy values as a result of irradiation.

As far as the authors are aware, there is little mention in the literature data including the electrical conductivity as a function of temperature and γ-radiation for the metal complexes studied here. Thus, the behaviour of electrical conductivity and the semiconducting properties of these materials as a function of temperature and γ-radiation doses appeared to be particularly promising in view of the large number of the available compounds of most transition metals with various substituted organic ligands, and due to the recent interest of metal complexes for their greater biological activity than their corresponding organic ligands.

EXPERIMENTAL

Material preparation

This includes preparation of the two organic ligands of *N*-2-pyridyl benzamide (bapH), *N,N'*-dibenzoyl-2,6-diaminopyridine (dbapH), and their corresponding Co(II), Ni(II) and Cu(II) complexes.

Preparation of N-*(2-pyridyl) benzamide (bapH)*

To 2-aminopyridine (0.4 mole) dissolved in pyridine (0.04 mole) of benzoyl chloride was added dropwise through a dropping funnel, with constant vigorous stirring, the temperature not exceeding 5° C. The material obtained was recrystallized from ether.

Preparation of N,N'*-dibenzoyl-2,6-diaminopyridine (dbapH)*

To 2,6-diaminopyridine (0.04 mole) dissolved in pyridine, 0.08 mole

TABLE 1

Properties of the ligands

Compound	Colour	M.p. (° C)	C(%)		H(%)		N(%)	
			Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
bapH	Pale brown	86	72.81	72.73	5.03	5.05	14.20	14.14
dbapH	Pale brown	174	56.00	55.96	5.72	5.69	21.52	21.76

TABLE 2

Analysis of N-(2-pyridyl) benzamide and *N,N'*-dibenzoyl-2,6-diaminopyridine complexes

Compound	M.p. (°C) (decomp. temp.)	M(%)		N(%)		X(%)	
		Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
$(bapH)_2NiCl_2$	270	11.16	11.00	10.65	10.53	26.02	26.00
$(bapH)_2NiBr_2$	283	9.54	9.50	9.11	9.20	35.66	35.60
$(bapH)_2Ni(NO_3)_2$	300	10.14	9.96	14.51	14.60		
$(bapH)_2CuCl_2$	230	11.97	11.86	10.65	10.60	13.38	13.30
$(bapH)_2Cu(NO_3)_2$	246	11.03	11.10	14.59	14.70		
$(dbapH)CoCl_2$	294	13.19	13.22	9.39	9.28	15.89	16.00
$(dbapH)CoBr$	296	10.99	11.00	7.84	7.73	29.83	29.90
$(dbapH)Co(NO_3)_2$	300	15.11	15.00	17.95	18.00		
$(dbapH)Co(NCS)_2$	300	11.98	12.00	14.23	14.10		
$(dbapH)_2NiCl_2$	291	7.68	7.69	10.99	11.00	9.29	9.30
$(dbapH)_2Ni(NO_3)_2$	200	7.18	7.20	13.71	13.63		
$(dbapH)_2Ni(NCS)_2$	300	7.26	7.30	13.84	14.00		
$(dbapH)CuCl_2$	263	14.06	14.00	9.30	9.36	21.67	21.58
$(dbapH)CuBr_2$	281	11.75	11.78	7.77	7.68	38.44	38.52
$(dbapH)Cu(NO_3)_2$	273	12.58	12.60	13.87	13.90		

benzoyl chloride was added dropwise, the temperature not exceeding 5°C during the addition. The material was recrystallized from a benzene—alcohol mixture.

Following preparation, elemental analyses, colour and melting points of the organic ligands obtained were carefully determined in each case and are shown in Table 1. Further experiments, NMR, IR and UV, were carried out to ensure their highest purity and individuality.

Preparation of the corresponding metal chelates

All the corresponding metal chelates of Co(II), Ni(II) and Cu(II) complexes under investigation were prepared as follows. To a cold solution of MX_2 where M = Co(II), Ni(II) and Cu(II), and X = Cl^-, NO_3^-, ClO_4^- in ethanol (0.01 mole), 0.02 mole of the organic ligand in ethanol (10 ml) was added with shaking. The corresponding crystalline precipitates were separated, filtered off, washed several times with ethanol and then dried over P_2O_5 in a vacuum desiccator for 24 h. For X = Br^-, I^-, and SCN^-, the corresponding complexes were prepared by the addition of equivalent amounts of ammonium bromide, ammonium iodide and ammonium thiocyanate. The elemental analyses and melting points are given in Table 2. Following analysis, NMR, IR and UV spectra measurements were undertaken to ensure the formation and individuality of the different metal complexes.

Electrical conductivity measurements

In this investigation, the purified and dried metal complexes were ground and compressed at 400 kg cm^{-2}, using a stainless steel mould and a hydraulic press, in the form of disks 1.22 cm in diameter and 0.20—0.40 cm thick. The applied pressure of 400 kg cm^{-2} is used at which the grain boundary effect is negligible and conductivity is independent. The circuit used is very similar to that previously devised by Owen [9], with some modification. The sensitivity of the electrometer used is 0.2%. Measurements were performed at room and elevated temperatures up to 388 K under an applied potential of 200 V.

γ-*Irradiation*

For irradiation studies, the specimens were irradiated using a ^{60}Co γ-cell (The Midle East Centre of Radioactive Isotopes, Dokki, Giza, Egypt.), at room and elevated temperatures for 10^7—10^{10} rads (at temperatures up to 388 K to simulate the conditions of the conductivity measurements).

RESULTS AND DISCUSSION

Effect of temperature on the electrical conductivity

The variations of electrical conductivity of Cu(II) and Ni(II) complexes of bapH and dbapH with the reciprocal of the absolute temperature in the temperature range 293—388 K are represented graphically in Figs. 1—5. Straight line relations were obtained from which log σ_0, log σ_{25}, activation energy (E), and energy gap ($2E$) were calculated and are given in Table 3. The behaviour shows a positive temperature coefficient of electrical conductivity, indicating that semiconducting behaviour or promotion of electrons from the ground to the excited states may occur [10].

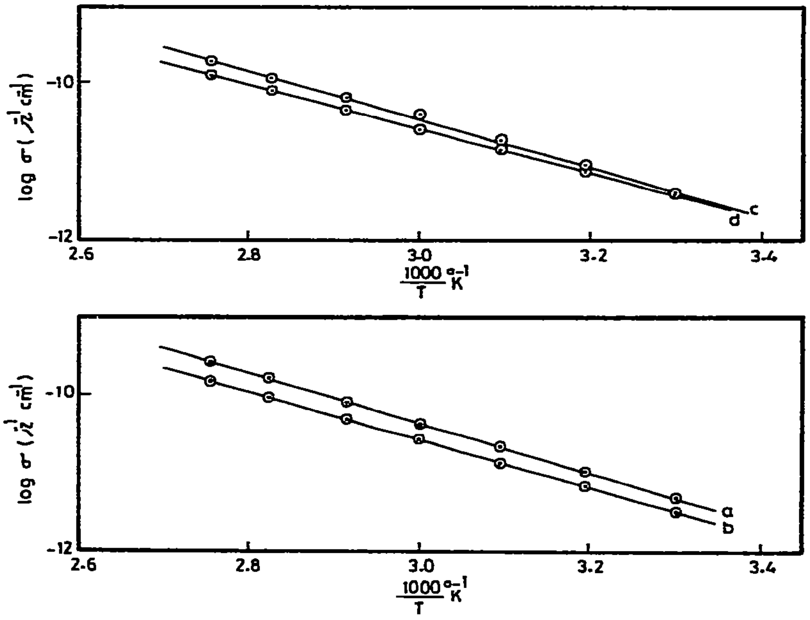
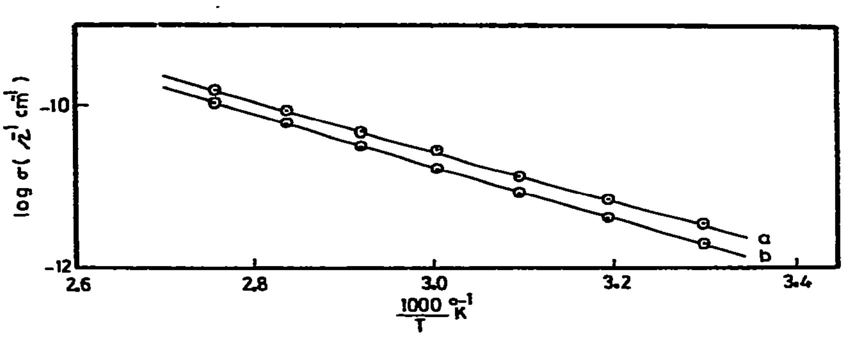


Fig. 1. The variation of log σ with $1/T$ before γ-irradiation of (a) $[(dbapH)CoCl_2]$; (b) $[(dbapH)CoBr_2]$; (c) $[(dbapH)Co(NO_3)_2]$; (d) $[(dbapH)Co(NCS)]$.



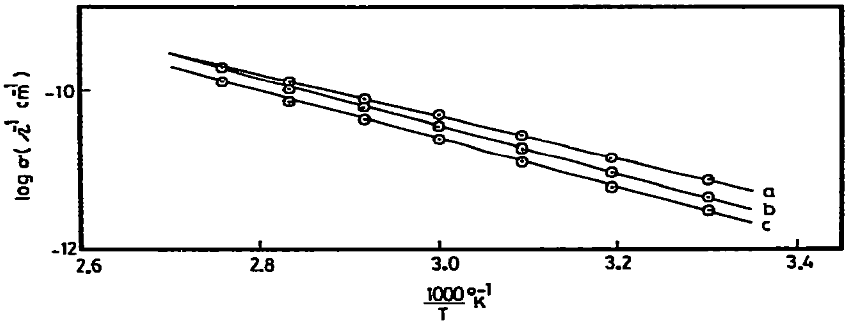
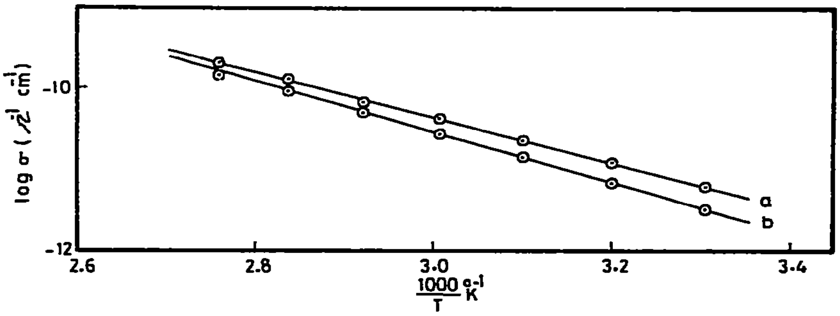


Fig. 2. The variation of log σ with $1/T$ before γ-irradiation of (a) [$(dbapH)_2NiCl_2$]; (b) [$(dbapH)_2Ni(NCS)_2$] and [$(dbapH)_2Ni(NO_3)_2$].

Fig. 3. The variation of log σ with $1/T$ before γ-irradiation of (a) [$(dbapH)CuCl_2$]; (b) [$(dbapH)CuBr_2$]; (c) [$(dbapH)Cu(NO_3)_2$].



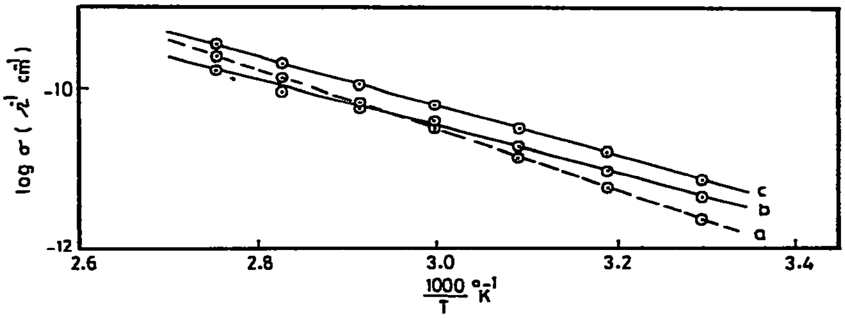


Fig. 4. The variation of log σ with $1/T$ before γ-irradiation of (a) [$(bapH)_2CuCl_2$]; (b) [$(bapH)_2Cu(NO_3)_2$].

Fig. 5. The variation of log σ with $1/T$ before γ-irradiation of (a) [$(bapH)_2NiCl_2$]; (b) [$(bapH)_2NiBr_2$]; (c) [$(bapH)_2Ni(NO_3)_2$].

TABLE 3

Values of activation energy, E, energy gap, $2E$ [11], and electrical conductivity, σ, of (dbapH) and (bapH) complexes

Complex	E (eV)	$2E$ (eV)	$\log \sigma_0$	$\log \sigma_{25}$
$\mathrm{(dbapH)CoCl_2}$	1.25	2.5	-1.20	-11.45
$\mathrm{(dbapH)CoBr_2}$	1.26	2.52	-0.80	-11.60
$\mathrm{(dbapH)Co(NO_3)_2}$	1.28	2.56	-1.20	-11.50
$\mathrm{(dbapH)Co(NCS)_2}$	1.10	2.20	-2.20	-11.50
$\mathrm{(dbapH)_2NiCl_2}$	1.37	2.74	-0.8	-11.90
$\mathrm{(dbapH)_2Ni(NO_3)_2}$	1.32	2.64	-0.4	-11.50
$\mathrm{(dbapH)_2Ni(NCS)_2}$	1.19	2.38	-0.40	-11.70
$\mathrm{(dbapH)CuCl_2}$	1.22	2.44	-1.30	-11.25
$\mathrm{(dbapH)CuBr_2}$	1.22	2.44	-1.10	-11.60
$\mathrm{(dbapH)Cu(NO_3)_2}$	1.22	2.44	-0.60	-11.65
$\mathrm{(bapH)_2CuCl_2}$	1.46	2.92	-4.10	-11.35
$\mathrm{(bapH)_2Cu(NO_3)_2}$	1.22	2.44	-1.80	-11.65
$\mathrm{(bapH)_2NiCl_2}$	1.37	2.74	-0.90	-11.80
$\mathrm{(bapH)_2NiBr_2}$	1.25	2.50	-0.60	-11.50
$\mathrm{(bapH)_2Ni(NO_3)_2}$	1.20	2.40	-0.70	-11.30

The present measurements and calculations (Table 3) are based on the mathematical expression [12]

$$\sigma = \sigma_0 \exp^{-\Delta E/2KT}$$

where σ is the specific conductivity, σ_0 is a constant independent of temperature, K is Boltzmann's constant, and ΔE is the activation energy (eV).

Since all Co(II) and Ni(II) complexes are insoluble in most solvents, they may be considered as polymeric. Thus, the interaction might occur between adjacent atoms in the metal chain (the metal chain complexes have been a topic of considerable recent interest [13,14]). Accordingly, the results obtained indicated that in all cases relatively higher conductivities and lower activation energies were obtained, in accordance with results of Jacobs [13].

Applying the method of Teuerstein et al. [4], the carrier mobilities, μ, of different complexes were found to be in the range 10^{-6}—10^{-10} cm^2 V^{-1} sec^{-1} and increases with increase in temperature. According to Glarum [14], values of μ which are smaller than 1 cm^2 V^{-1} sec^{-1} and which increase with temperature might be used as a criterion for applying the hopping model for describing the conduction mechanism as in the present investigation.

It is evident that in most cases high activation energy and low electrical conductivity are associated with a high ligand-to-metal ratio (see Table 3). This may be attributed to the fact that the metal atoms act as a bridge facilitating the transfer of current. Thus one can assume that the first step in the conduction process is the excitation of Π electrons from the upper filled Π orbitals to the lowest empty Π MO. The electrons are then assumed to tunnel to the equivalent empty level of the neighbouring molecule in the direction of the anode, whereas the positive holes are moving to a molecule in the opposite direction towards the cathode. It is possible to adopt this model for a discussion of the mechanism of conduction of the investigated metal complexes, but it must be noted that there are some difficulties necessitating modification of the model to some extent. If the initial excitation is caused by the complexes it is no longer necessary that the electron in the uppermost Π level comes from the highest occupied Π MO. It would also arise from an orbital essentially localized on the metal atom and this would result in the generation of an essentially immobile positive centre. In addition, it is conceivable that electron transport is facilitated by the greater surface of the molecule which would produce stronger intermolecular interactions and consequently narrower barrier widths.

The relatively low activation energy and high electrical conductivity for complexes containing NCS$^-$ ions (see Table 3) can be attributed to the greater affinity of crosslinking for NCS$^-$ complexes. In this case, crosslinking is more liable due to the localized lone pair of electrons of the sulphur atom in accordance with that given by Schrauzer et al. [3,15] denoting that the unsaturated C=S system is capable of facilitating electron transfer and current flow. In summary, it was concluded that the magnitude of the electrical conductivity in the transition metal chelates is highly dependent on the extent of Π delocalization of electronic structure.

Effect of γ-irradiation on the electrical conductivity

Cu(II), Co(II) and Ni(II) complexes derived from (bapH) and (dbapH) ligands were irradiated with γ-rays at different doses. The variation of DC electrical resistivity of these complexes with γ-radiation doses of up to 10^{10} rads are evaluated. Since all of the investigated Co(II), Ni(II) and Cu(II) com-

TABLE 4

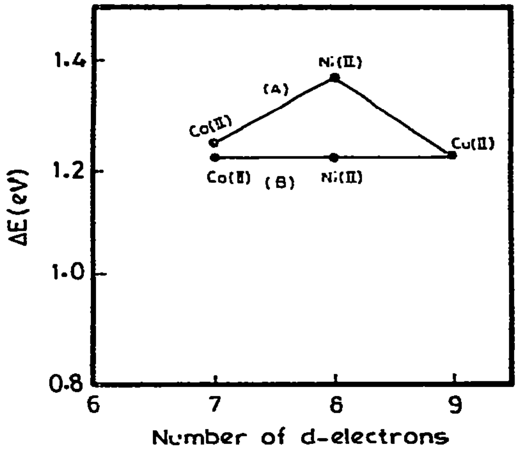
Values of activation energy, E, energy gap, $2E$, and electrical conductivity, σ, of (dbapH) and (bapH) complexes after irradiation (10^9 rads)

Complex	E (eV)	$2E$ (eV)	log σ_0	log σ_{25}
(dbapH)CoCl$_2$	1.22	2.44	−1.20	−11.45
(dbapH)CoBr$_2$	1.22	2.44	−2.20	−11.55
(dbapH)Co(NO$_3$)$_2$	1.23	2.46	−3.10	−11.30
(dbapH)Co(NCS)$_2$	1.13	2.26	−0.70	−11.75
(dbapH)$_2$NiCl$_2$	1.22	2.44	−3.00	−11.75
(dbapH)$_2$Ni(NO$_3$)$_2$	1.21	2.42	−2.30	−11.35
(dbapH)$_2$Ni(NCS)$_2$	0.95	1.90	−4.00	−11.15
(dbapH)CuCl$_2$	1.22	2.44	−2.40	−11.25
(dbapH)CuBr$_2$	0.92	1.84	−3.68	−11.35
(dbapH)Cu(NO$_3$)$_2$	1.09	2.18	−2.40	−11.20
(bapH)$_2$CuCl$_2$	0.86	1.72	−4.30	−10.09
(bapH)$_2$Cu(NO$_3$)$_2$	0.99	1.98	−2.80	−11.05
(bapH)$_2$NiCl$_2$	0.95	1.90	−3.75	−11.10
(bapH)$_2$NiBr$_2$	0.96	1.92	−3.40	−11.35
(bapH)$_2$Ni(NO$_3$)$_2$	1.06	2.12	−2.20	−11.30

plexes are insoluble in most organic solvents, Co(II) and Ni(II) complexes remain polymeric in nature (as before irradiation), and Cu(II) complexes acquire γ-irradiation induced polymerization via a free radical and crosslinking mechanism.

It can be seen that complexes having X = Cl^-, Br^-, NO_3^- exhibit similar behaviour in the sense that their resistivity is slightly affected by γ-doses up to 10^{10} rads, indicating their greater resistance and higher stability than for the others. At 10^7 rads, the three Ni(II) complexes behave in similar manner to Cu(II) complexes. Above 10^9 rads, their resistivity decreases, reaching a constant value, indicating that the number of created charges is equal to the number of carriers lost. The variation of electrical conductivity of the afore-mentioned Cu(II), Co(II) and Ni(II) complexes with the reciprocal of the absolute temperature ($\log \sigma$ vs. $1000/T$) after irradiation with 10^9 rads are evaluated and depicted in terms of $\log \sigma_0$, $\log \sigma_{25}$, ΔE and energy gap (Table 4). The afore-mentioned description indicates that γ-irradiation alters the resistivity of the investigated materials in the sense that irradiation damage may take place.

The observed increase in electrical conductivity of some metal chelates can be explained according to Vinyard and Pienes [16], proposing that the primary effects of ionizing radiation consists in displacing positive metal ions and electrons. Under the field produced by the surrounding lattice ions, it moves into an interstitial position. In this way, a considerable number of negative vacancies may be produced which introduces impurity levels. These levels serve as recombination levels for electrons and thus cause a considerable decrease in current. This means that the conductivity of some divalent metal complexes approaches the value of pure organic ligands. This can be related to the rupture of the metal ligand bonds with the production of free ligand molecules as a result of γ-radiation damage [8]. On the other hand, the observed increase in electrical conductivity and decrease in activaiton energy



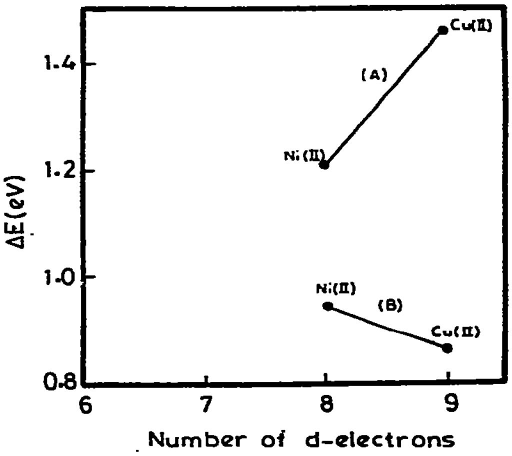


Fig. 6. The variation of ΔE with the number of d electrons of the transition metal cations in $[(dbapH)_nMCl_2]$ complexes (A) before irradiation and (B) after irradiation (10^9 rads).

Fig. 7. The variation of ΔE with the number of d electrons of the transition metal cations in $[(dbapH)_2MCl_2]$ (A) before irradiation and (B) after irradiation (10^9 rads).

in some cases as a result of γ-irradiation (see Tables 3 and 4) may be attributed to the fact that the effect of γ-irradiation in a semiconductor is significant in displacing atoms from equilibrium positions.

On prolonged irradiation many vacancies and interstitial atoms are created [17]. The propagation of these defects may result in partial dissociation and/or recombination of the different metal complexes giving rise to donor impurities. The extent of irradiation damage is quite different for the different complexes. This is in accordance with the finding of Viadiminskii and Nikitinskaya [18] that the change in electrical resistivity of a semiconductor after irradiation depends primarily on the degree of lattice defects that are originally present in the sample before irradiation.

The variation of ΔE (eV) of the prepared metal complexes of (dbapH) and (bapH) ligands with the number of "*d*" electrons of Cu(II), Co(II) and Ni(II) before and after γ-radiation (10^9 rads) is shown in Figs. 6 and 7, respectively. The lower value of the activation energy of (dbapH)$CuCl_2$ than those of the corresponding Co(II) and Ni(II) complexes can be correlated with its square-based pyramidal structure and d^9 electrons which is not the case for Co(II) complexes (tetrahedral, d^7) and Ni(II) complexes (octahedral, d^8). Lowering of the ΔE value (see Fig. 6) for Co(II) and Ni(II) complexes and the constancy of the ΔE value for the Cu(II) complex before and after irradiation might be explained by the fact that Co(II) and Ni(II) complexes are highly polymerized and/or undergo further induced crosslinking and polymerization by γ-irradiation.

Before γ-irradiation, the diagrammatic representation in Fig. 7A shows that the Cu(II) complexes have higher ΔE values than Ni(II) complexes and this may be due to the nonpolymeric nature of Cu(II) complexes [19]. After γ-irradiation (Fig. 7B), the lowering of ΔE for Cu(II) to a value below that of Ni(II) complexes may be due to the effect of γ-irradiation crosslinking, offering an easier way for current transfer across the high molecular weight branched polymer of the Cu(II) complex. This is in accordance with the insolubility of Cu(II) complexes after irradiation as being correlated with the polymeric nature of the product as affected by γ-irradiation.

CONCLUSIONS

From the above results and discussion, the following conclusions are made.

(1) A sequence, including the relative stability of the investigated metal complexes towards the effect of γ-irradiation at the initial dose (10^7 rads) is proposed: (a) $[(dbapH)CoX_2] > [(dbapH)_2NiX_2] > [(dbapH)CuX_2]$; (b) $[(bapH)_2NiX_2] > [(bapH)_2CuX_2]$.

(2) Generally, Co(II) and Ni(II) complexes are more stable than their corresponding isostructure Cu(II) complexes. This was correlated with the ligand field strength as their stability is further increased at stronger ligand field.

(3) The originally polymeric metal complexes possess a higher resistance towards γ-irradiation damage then for the nonpolymeric ones.

(4) As a result of γ-irradiation, the nonpolymeric Cu(II) complexes of (dbapH) and (bapH) ligands may undergo induced polymerization through crosslinking, as established from conductivity and solubility measurements.

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