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EFFECT OF TEMPERATURE AND ABSORBED IONIZING RADIATION DOSES ON THE ELECTRIC AND ELECTRONIC PROPERTIES OF COPPER(II) COMPLEXES

M.M. ABOU SEKKINA, A. EL-DISSOUKY
Department of Chemistry, Faculty of Science, Tanta University, Tanta (Egypt)

M. OSMAN
Alexandria University, Alexandria (Egypt)

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ABSTRACT

A large number of copper(II) complexes derived from their related pyridine derivatives were prepared, crystallized and their characteristics established. The temperature dependence of d.c. electronic (electrical) conductivity and the electronic absorption properties of the materials under investigation were studied before and after exposure to various absorbed gamma doses up to 10^7 rads using a ^{60}Co gamma cell. The effect of gamma absorbed doses on the d.c. electrical conductivity and electronic absorption spectra of γ-irradiated samples are discussed on the basis of the effect of ionizing radiation firstly on metal–oxygen, and secondly on C–C bonds regarding the substituent effect on their electronic delocalization and their geometrical structures.

INTRODUCTION

Pyridine derivatives with suitable donor atoms in the 2-position can be used as chelating agents. These kinds of compounds in which the side chain contains an amide group have been shown to coordinate the metal ions via the pyridine-nitrogen atom and either the nitrogen or oxygen of the amide group [1–4]. The investigation was originally stimulated by the suggestions of Szent-Gyorgi [5] on the possible role of mobile electrons in protein molecules, but until now work has been directed mainly towards the examination of simpler and more thermally stable molecules. A semiconductivity has been observed for phthalocyamine by Vartainian [6], and for various condensed rings by Akamatu and Inokuchi [7–9]. Gomm et al. [10] studied the electrical conduction of single crystals of transition metal complexes deducing a highest conductivity in the direction of the metal-atom chain.

In irradiation with ^{60}Co γ-rays, the Compton effect has the largest

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cross-section [11] except for materials of very high atomic number and, moreover, the number of atoms displaced (cm^{-3} s^{-1}) is the maximum in the very light elements and diminishes [12] to zero around atomic weight 125. Irradiation with these rays therefore includes atomic displacements by the Compton electrons. Photoelectric and pair production events appear. As far as the authors are aware little mention is found in the literature data concerning the effect of gamma absorbed doses on these materials.

In view of the large number of available compounds of most transition metals with unsubstituted and various substituted organic ligands, the aim of the present work is to throw light on the electrical and electronic properties of some selected solid copper(II) complexes induced by gamma absorbed doses.

EXPERIMENTAL

Material preparation

The investigated organic ligands and their corresponding ccpper(II) complexes were prepared, crystallized and their structures evaluated in a previous work [13].

D.c. electrical conductivity measurements

A two-probe method was employed using graphite paste electrodes as contacts. A compact furnace surrounded the specimen and all measurements were made in air as it was known that there was no risk of oxidation throughout the temperature range investigated. The current (I) was measured directly using a galvanometer (sensitivity 0.009 μA/mm deflection). With a suitable constant voltage (V) applied, the conductivity was driven from

$$\sigma = \frac{d}{A} \times \frac{I}{V}$$

where d and A, the length and cross-sectional area, respectively, were obtained accurately from the measured dimensions of the rectangular specimen. The experimental arrangement and measuring technique were similar to those previously described by Alzewel et al. [14]. Measurements were taken at room and elevated temperature up to $\simeq 370$ K.

Electronic absorption spectra measurements

A Unicam SP 8000 spectrophotometer was employed. The Nujol mull spectra were obtained according to the method of Lee et al. [15]. Measurements were made in the range 200–450 (mμ).

Gamma radiation exposure

The materials were exposed to various absorbed doses up to 10^7 rads using a ^{60}Co cell in air at room temperature. The measurements were conducted soon after removing the specimen from the radiation field.

RESULTS AND DISCUSSION

Representative figures only are given to cover the most common features of all material investigated.

Figure 1 (curve a) shows the variation of d.c. electrical conductivity as a

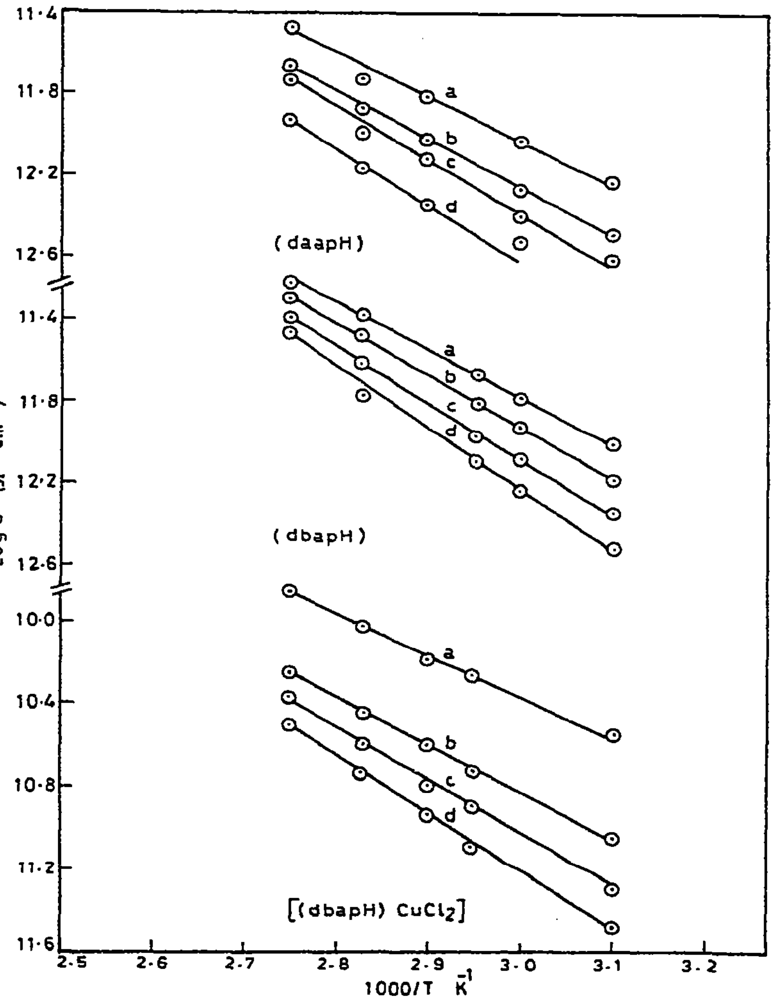

Fig. 1. The temperature dependence of d.c. electrical conductivity at various absorbed gamma doses for (daapH), (dbapH) and [(dbaph)CuCl$_2$]. (a) Before irradiation; (b) after the first absorbed dose (10^3 rads); (c) after the second absorbed dose (10^5 rads); (d) after the third absorbed dose (10^7 rads).

function of temperature before radiation exposure for two organic ligands of *N*,*N'*-diacetyl-2,6-diaminopyridine (daapH), *N*,*N'*-dibenzoyl-2,6-diaminopyridine (dbapH) and the copper(II) complex of dichloro-*N*,*N'*-dibenzoyl-2,6-diaminopyridine [(dbapH)CuCl$_2$]. This corresponds to the behaviour often observed in semiconductor compounds and the conductivity varies with temperature exponentially according to the well-known relation [14]

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

The slight response of σ to temperature variation in the lower temperature intervals of the plots involves ΔE values which can be interpreted by a simple single band model in most compounds. Values of ΔE are calculated as 0.80 and 0.48 eV for the (dbapH) organic ligand and its corresponding copper(II) complex [(dbapH)CuCl$_2$] respectively, and are assumed to correspond to the activation energies of defect mobilities.

As a general feature, the electrical conductivity increases and the activation energy decreases on passing from the pure organic ligand to its copper(II) complex. This may be explained on the basis that the metal ion may act as a bridge facilitating the flow of current [10] through the organic ligand molecules. As a general trend among the investigated organic ligands, the electrical conductivity increases and the activation energy decreases as a function of donor substitution and replacement of the methyl group with the phenyl group. This is most probably correlated with an increased electron delocalization on the whole molecule in the case of the phenyl group (which has conjugated π electrons). Accordingly, it is suggested that the excited orbitals of the π electrons in the isolated molecule are combined to give non-localized orbitals stretching throughout the crystals. $2\Delta E$ is then the energy gap (Table 1) between the highest filled band or molecular level and the conduction band. Its value can be discussed in terms of single electron transitions in the isolated molecule, and the overlap of π orbitals between neighbouring molecules.

TABLE 1

Energy gap ($2\Delta E$) values (eV) obtained at various gamma absorbed doses for some of the investigated materials

Material	Absorbed doses (rads)			
	0	10^3	10^5	10^7
daapH	1.92	2.00	2.16	2.24
dbapH	1.60	2.00	2.24	2.32
[(dbapH)CuCl$_2$]	0.96	1.36	2.00	1.68
[(aapH)$_2$CuBr$_2$]	1.52	1.76	2.24	2.00

Figure 1 (curves b, c and d) represents the temperature dependence of d.c. electrical conductivity at various absorbed gamma doses up to 10^7 rads for daapH, dbapH organic ligands and the copper(II) complex (dbapH)CuCl$_2$. The same plot was undertaken under the same conditions for square pyramidal and octahedral copper(II) complexes [see Fig. 2 (curves b, c and d)].

From the results obtained (Figs. 1 and 2), the following deductions were made.

(1) For the investigated organic ligands the d.c. electrical conductivity decreases and the activation energy for conduction increases as a function of energy of the absorbed dose. This may be correlated with the partial destruction of the material along the C–C bond [16] as a result of radiation damage leading to restriction of the electronic delocalization of the π electrons. This explanation is established by the pronounced effect of the absorbed gamma doses on dbapH containing the phenyl group instead of the $-CH_3-$ group [see Fig. 1 (curve b)].

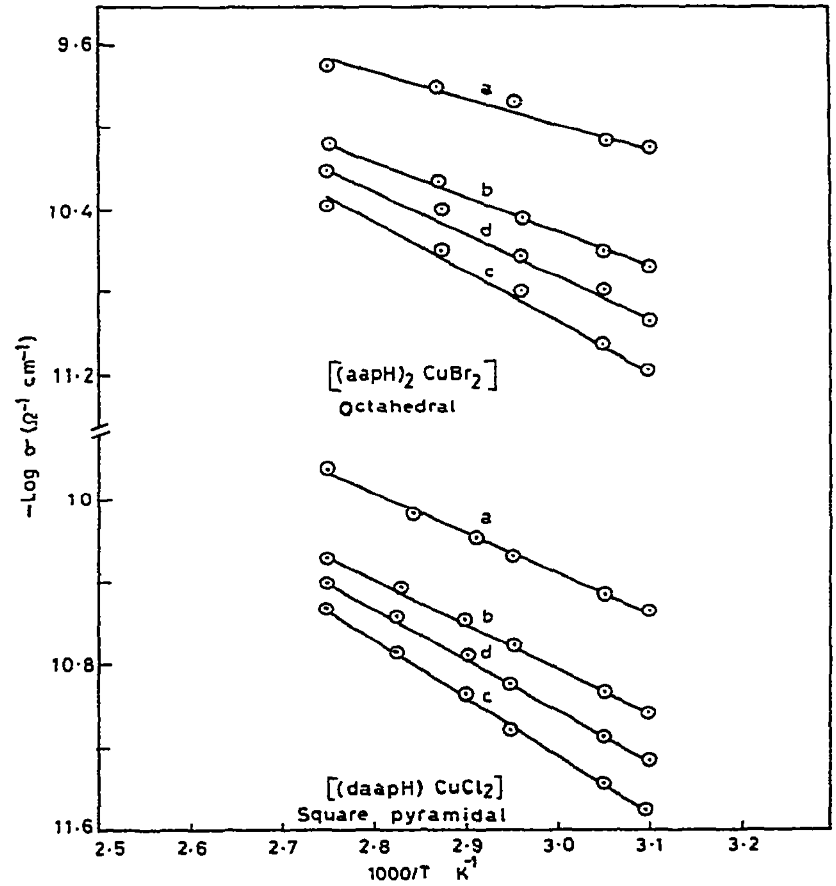

Fig. 2. The temperature dependence of d.c. electrical conductivity at various absorbed gamma doses for square pyramidal [(daapH)CuCl$_2$] and octahedral [(aapH)$_2$CuBr$_2$]. (a) Before irradiation; (b) after the first absorbed dose (10^3 rads); (c) after the second absorbed dose (10^5 rads); (d) after the third absorbed dose (10^7 rads).

(2) For the investigated copper(II) complexes the d.c. electrical conductivity decreases and the activation energy for conduction increases as a function of absorbed gamma doses up to a definite dose dependent on the geometrical structure and substituent effect of the organic component followed by a reversal in behaviour at the subsequent higher absorbed dose. This behaviour could be explained on the basis that the gamma absorbed dose may lead to a partial destruction along the chelate bond at the initial stages followed by cross-linking and/or creation of a free radical causing the observed increase in electrical conductivity and decrease in activation energy for conduction (see Fig. 3 and Table 2) at the highest absorbed dose.

(3) For the octahedral copper(II) complex (Fig. 2) the gamma absorbed dose damage has a more consistent effect than the corresponding square pyramidal complex (Fig. 2), this could probably be attributed to the existence of a larger number of chelate bonds for octahedral copper(II) complexes which are more susceptible to radiation damage than those of the square pyramidal copper(II) complexes.

Figures 4 and 5 show the effects of gamma absorbed doses on the electronic absorption spectra of the investigated daapH organic ligand and copper(II) complex derived from the dbapH ligand, respectively. As a result of gamma absorbed doses, the characteristic features of all the investigated materials are:

(a) a gradual shift towards longer wavelength (red shift) as a function of the absorbed dose, accounting for the fact that the decomposition product may undergo electronic transition at lower energy, and/or atomic displacement [12] may occur;

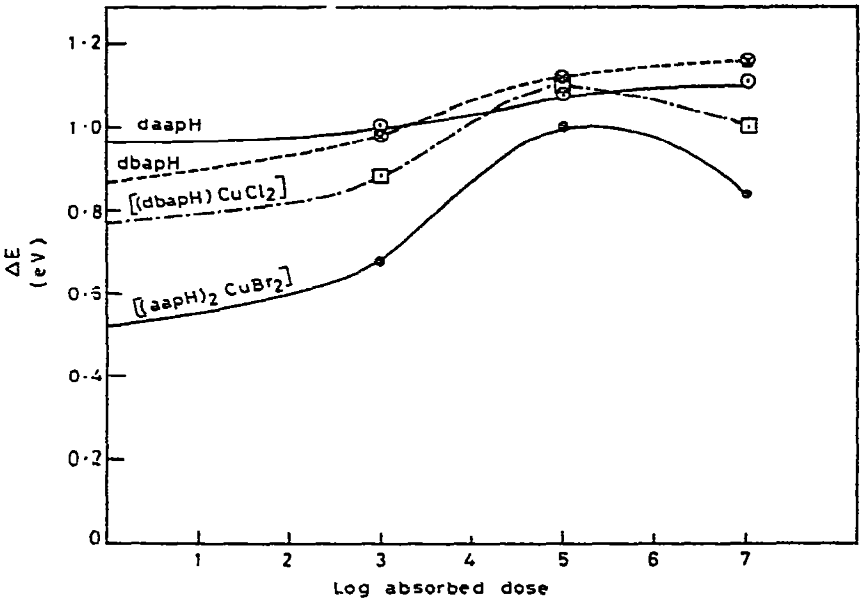

Fig. 3. The variation of activation energy for conduction (eV) as a function of the absorbed gamma doses for some of the investigated materials.

TABLE 2

ΔE values (eV) obtained at the various gamma absorbed doses for some of the investigated materials

Material	Log absorbed dose (rads)			
	0	3.00	5.00	7.00
daapH	0.96	1.00	1.08	1.12
dbapH	0.80	1.00	1.12	1.16
$[(\mathrm{dbapH})\mathrm{CuCl}_2]$	0.48	0.68	1.00	0.84
$[(\mathrm{aapH})_2\mathrm{CuBr}_2]$	0.76	0.88	1.12	1.00

(b) a gradual broadening and decreasing of the intensity of the absorption bands as a function of energy of the radiation dose;

(c) some bands are created and others completely disappear as a function of the absorbed doses. These changes are found to be more pronounced in the case of copper(II) complexes than for the organic ligands.

Thus results for the effects of radiation on d.c. electrical conductivity are in agreement with those of radiation effects on the characteristic features of the electronic absorption spectra. This is most probably explained by the increased electronic delocalization which is more susceptible to radiation damage for copper(II) complexes than for the isolated organic ligands. However, when gamma rays attack semiconductors or insulators a large

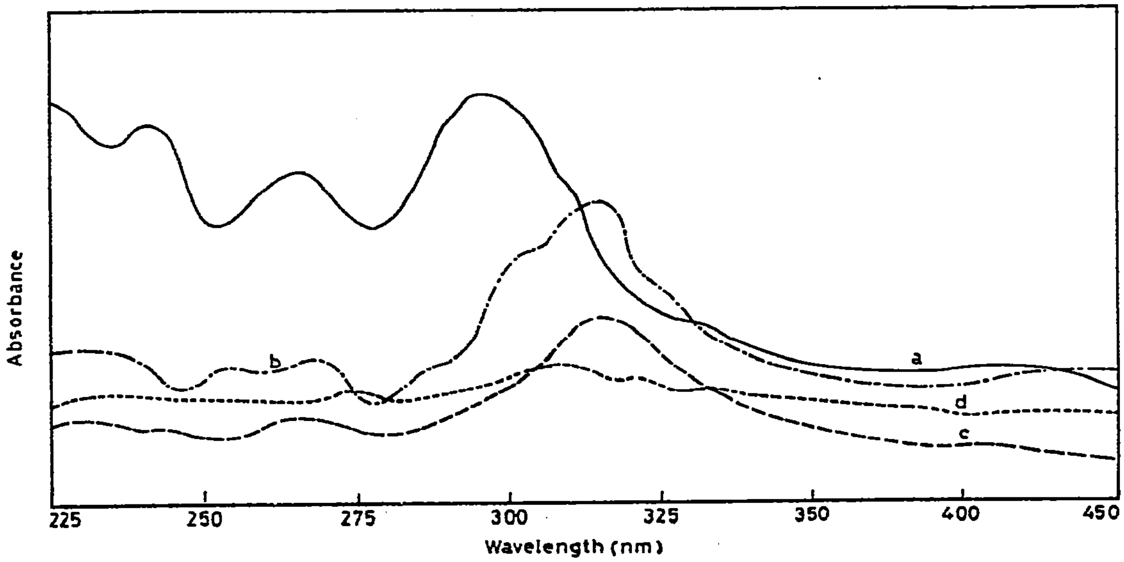

Fig. 4. The electronic absorption spectra of (daapH). (a) Before irradiation; (b) after the first radiation dose (10^3 rads); (c) after the second radiation dose (10^5 rads); (d) after the third radiation dose (10^7 rads).

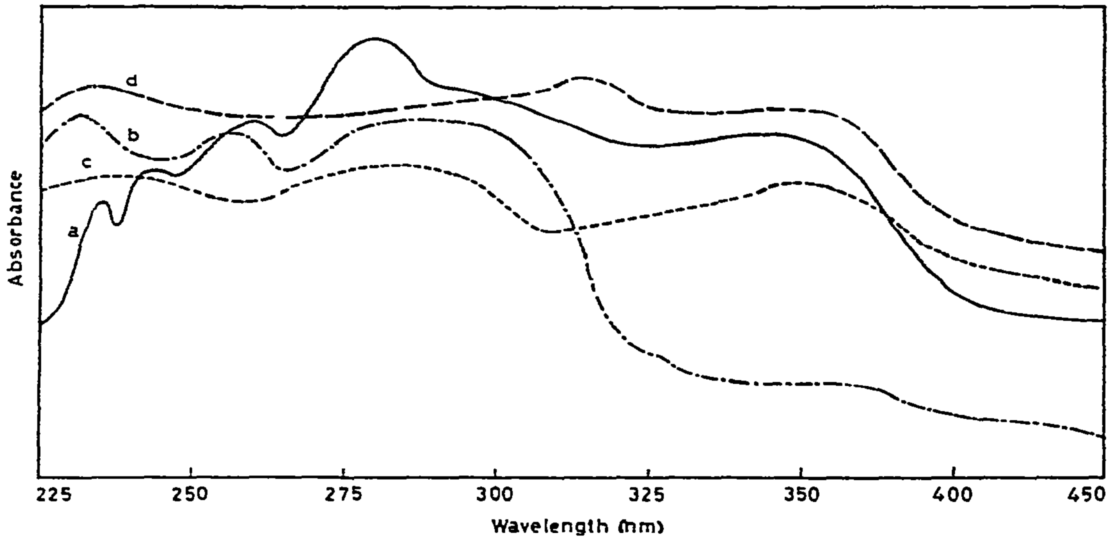

Fig. 5. The electronic absorption spectra of [(dbapH)CuCl$_2$]. (a) Before irradiation; (b) after the first radiation dose (10^3 rads); (c) after the second radiation dose (10^5 rads); (d) after the third radiation dose (10^7 rads).

number of electrons along with electron deficient regions, commonly called holes, are thus produced. The large majority of the freed electrons recombine with the holes within a very short time. However, some electrons and holes may become trapped for long periods, especially at lower temperatures. Intrinsic defects (lattice defects or impurities) act as trapping sites. As a result, the irradiated materials will have regions with excess trapped electrons (electron trap centres) normally at negative ion vacancies and other regions which are deficient in electrons (positive hole centres). These new electronic configurations may cause preferential light absorption at particular wavelengths and hence are known as "colour centres". Over the induction period, the point defects aneal out and the energy released at the site of recombination results in the formation of decomposition nuclei [17] in addition to those induced upon irradiation.

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