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On Coordination of Secondary Cu(II) Dithizonate Complex†

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Secondary Cu(II) dithizonate complex was synthesised as solid from corresponding benzene-aqueous phase. IR,LF (ligand field), ESR and mass spectra together with thermal and elemental analysis of the complex were carried out. Generally, the spectral results suggested an approximately square planar coordination of copper ions, possibly with supplementary axial ligands. Moreover, the calculated value of G, 3.8, indicated the presence of some exchange coupling. However, the molecular structure of the complex is discussed in view of IR results as well as the computed spectroscopic g and $\triangle$ values.

INTRODUCTION

Despite the importance of dithizone (3-mercapto-1,5-diphenylformazan, Ph—N=N—CS—NH—NH—Ph, H_2Dz) in many fields of application such as trace metal analysis and the utilization of some of its metal complexes in solar batteries, the molecular structure of many secondary dithizonates are not clear. On the other side the structure of many primary M(II) dithizonates (e.g. M(II)=Cu & Ni) were established by different methods[1,2]. However, secondary Cu(II) dithizonate is one which was extensively investigated, but discrepancy is still existing among the results of many authors. Freiser and Freiser[3] reported after various chemical arguments[4] that secondary Cu(II) dithizonate was a derivative of copper(I)[3], a view which was shown to be incorrect[4]. However, Alsop[5] measured μ_{eff}. (0.63 B.M.) for analysed solid secondary Cu(II) dithizonate formulated as CuDz. Moreover there are two another types of formulae, namely, $CuDz.H_2O$ and $CuDz.2H_2O$ as found and proposed by many authors[6]. According to such results as well as that of IR spectrum, different structural formulae were suggested with little informations about metal-ligand bonding and the point symmetry effective on the metal ion.

It is, therefore, aimed in this article to recognise the nature of bonding to Cu(II) ions in its secondary dithizonate complex and hence the geometrical arrangement of dithizone moiety around Cu^{2+} utilizing different spectroscopic methods.

EXPERIMENTAL

Benzene, sodium perchlorate-perchloric acid buffer solutions and diphenylthiocarbazone (H_2Dz) were purified according to the methods

†IUPAC nomenclature: (1,5-diphenylthiocarbazonato-N,S)-Cu(II).

described in literature[7,8]. The melting point of the resulting pure dithizone was 169°C (decomp.). $Cu(NO_3)_2.6H_2O$ was a product of Merck.

Secondary Cu(II) dithizonate was prepared by shaking for 10 minutes —one lit. of 0.003M solution of purified dithizone in thiophene free benzene with one lit. of 0.003M aqueous solution of copper nitrate buffered at pH = 7.5 with perchloric acid-sodium perchlorate buffer solution, then the two phases were allowed to separate. The organic layer was separated and the bulk of solvent distilled off under mild reduced pressure at *ca* 40°C. The residual secondary copper dithizonate was washed thoroughly several times with water to remove unreacted metal salts followed by washing with benzene to remove unreacted dithizone. The ligand (H_2Dz) and the synthesised secondary copper dithizonate CuDz were subjected to elemental analysis.

Ligand (found: N=20.90, C=60.06 & H=4.37; calcd. N=21.86, C=60.91 & H=4.72).

Secondary copper(II) dithizonate complex: (found: N=17.08, C=50.11, H=3.12 & Cu=19.61%; calcd. N=17.64, C=49.12, H=3.17 & Cu=19.99%).

IR spectra were recorded using a Perkin-Elmer 577 spectrophotometer (KBr disc method). Mass spectrum was measured on Kratos MS 50 mass spectrometer provided with data system. Absorption of the ligand (H_2Dz) and secondary copper dithizonate (CuDz) in benzene were recorded using Carl Zeiss M4/QII spectrophotometer, whereas E 15-Varian spectrophotometer was used in measuring the EPR spectrum of copper complex in Q-band (=35 GHZ) using DPPH as inner standard.

RESULTS AND DISCUSSION

IR-spectra as well as assignment of some important IR-frequencies of dithizone and copper (II) complex are reported (Fig. 1 and Table 1). The absence of band in the region 3400 cm^{-1} indicates the absence of water in the complex contrary to previous observation[6].

Also, the absence characteristic frequencies of NH stretching and bending modes at 3380, 1530–1550 and 1440 cm^{-1} is an indication of the formation of secondary copper (II) complex (1 : 1 adduct). The disappearance of peaks at 1600 and 1250 cm^{-1} which are characteristic of C=S and N=N groups, respectively, is due to the formation of covalent Cu-S bond and coordination bonds between the two azo nitrogens and copper. The new peaks appeared at 1510, 1020, 920, 880, 850, 620, 445, 425 and 340 cm^{-1} are due to the formation of Cu-N and Cu-S covalent bonds together with Cu ← N coordination bonds. The presence of two singlet deformation vibration bonds (=C-H) in the phenyl groups at 775 and 685 cm^{-1} in case of secondary copper complex instead of two doublets at 760 and

TABLE 1

ASSIGNMENT OF SOME IMPORTANT FREQUENCIES (cm^{-1}) OF DITHIZONE (H_2Dz) AND SECONDARY COPPER (II) DITHIZONATE (CuDz)

H_2Dz	CuDz	Assignment
3380(w)	—	NH stretching, may be bonded or involved in thioketon-enol transformation
—	3015(w)	=CH stretching
2960(w)	—	None hydroden bonded SH
—	1695(w),1675(w)	C=C and/or C=N stretching
1699(sh)	—	N=N stretching
1590(m)	1590(vs)	C=C in aromatic ring
1530–1505(sh)	—	NH bending with some C=N character
—	1510	C=N stretching
1440(vs)	—	NH bending
1380(m)	—	=CH bending in phenyl group
1315(s)	1340(br),1310(br)	N-phenyl
1250(m)	—	C=S
1222(vs),1215(vs) 1170(vs),1140(vs) and 1090(w)	1190(m),1155(sh) 1130(br)	NCS
—	1020	C-S-Cu
—	920,880,850,445	Cu-ligand
760(vs), 680(vs),670(vs)	755(vs) 685(vs)	(C-H) in phenyl group
—	425	Cu-N[9]
—	340(w)	Cu-S[9]

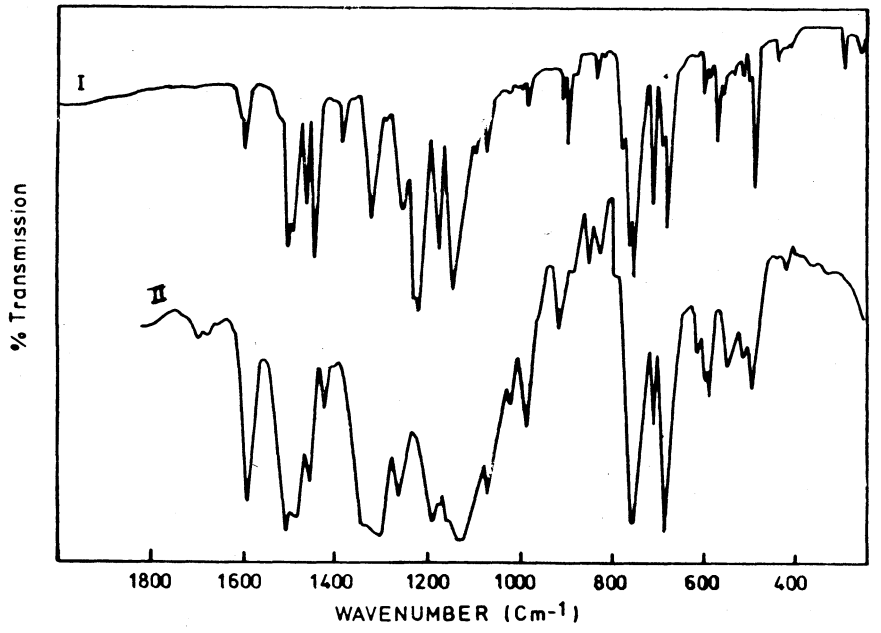
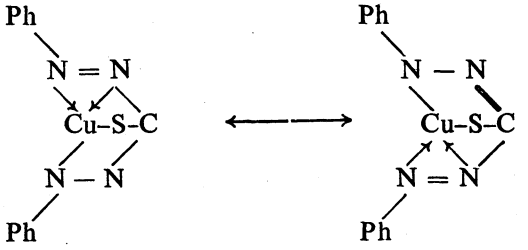


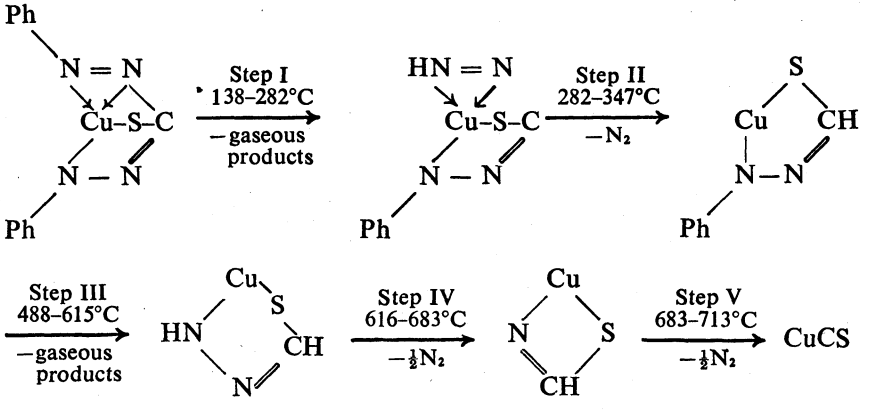
Fig. 1. IR-vibrational spectra of solid dithizone (I) and secondary copper dithizonate complex (II).

880; 750 and 670 for dithizone are in accord with the observation of Fabretti *et al.*[9], which means that the two phenyl groups in the complex are equivalent. Moreover, the decrease in intensity as well as the shift of NCS vibration bands in the spectrum of CuDz could be due to decrease of electrons delocalization throughout the dithizone residue as a result of complexation.

As gathered from elemental analysis and IR-results, the following structural molecular formula could be suggested:



Thermal gravimetry and differential thermal curves of secondary CuDz complex don't show any presence of water molecules in or out of the decomposition sphere. They also show that CuDz has five distinct regions of decomposition upto 715°C which could be formulated as follows:



It seems probably that the sequence of cleavage of bonds follows the order of their strength. Moreover, it was observed from the thermal curve that the fragment CuCS was not stable and decomposed above 713°C.

The mass spectra of dithizone and primary copper dithizonate[10] shows that both have peaks at (m/e)=77, 92, 93, 105, 150, 169 and 167 which are due to formation of ph·, phNH·, phNH·$_2$, phNN·, phNHNCS·, ph_2NH· and carbazole fragments, respectively. In the present work the secondary copper(II) dithizonate complex shows another route of splitting. The most important fragments are at (m/e) = 105, 150, 169, 212, 254 and 256 which

correspond to phN=N·, phNHN=C=S·, phN_2Cu· or ph_2NH, phN-N-C-S-Cu·, Dz·, and H_2Dz where Dz· is the base peak. The absence of peaks at (m/e) = 77, 92 and 93 which are responsible of the formation of ph·, $phNH_2$·, phNH and carbazole may be due to the presence of some copper organic fragments and secondary copper complex (m/e) = 318.

The electronic absorption spectrum of dilute solutions of CuDz in benzene shows a broad asymmetric *d-d* absorption band with a maximum at 17540 cm^{-1} together with a symmetric charge transfer one at 22720 cm^{-1} (Fig. 2). The low frequency *d-d* band could be assigned as the transition: $^2B_{1g}(^2E_g) \rightarrow {}^2A_{1g}(^2E_g)$ by assuming a strong Jahn-Teller distortion of ^2E_g ground state of Cu^{2+} in an octahedral coordination. Such strong disortion leads occasionally—via tetragonal elongation (D_{4h}) and square-based pyramidal configuration (C_{4v})—to a square planar coordination (D_{4h}) as an extreme case. Accordingly, the $^2A_{1g}$ splitterm may be thus considered to lie within the energy region of the splitterm ^2E_g ($^2T_{2g}$), a behaviour characteristic of square planar coordination as reported previously[11–14]. However, the energy position of the $^2A_{1g}$ splitterm with respect to that higher $^2E_g(^2T_{2g})$ depends usually upon the degree of Jahn-Teller distortion. In some cases some higher or lower energy values for such transitions were also observed. Generally, the measured absorption band centered at 17540 cm^{-1} (570 mμ) is quite comparable to those reported for some complexes, where a square planar symmetry of equitorial plane was assumed[15]. The shape of the powder EPR spectra of the Cu(II) complex at room temperature as well as at low temperature agrees, generally, with an axially elongated tetragonal geometry around Cu(II) with orthorhombic symmetry or lower (Fig. 3). At room temperature, the presence of orthorhombic components superimposed in the perpendicular component g_1[g_1 iso = 1/3(2.027 + 2.039 + 2.05) = 2·039] suggest a lowering of the equatorial symmetry, whereas the parallel component g_{11} shows no hyperfine splitting. The behaviour at lower temperature seems to be more likely the same with the only observation that the equatorial plane appears to be less distorted [g_1 iso = 1/2(2.032 + 2.040) = 2.036 indicating, however, that the distortion of the single CuN_3S polyhedron is still present even at lower temperature. The present g_1 iso value (2.036–2.039) is in a fairly agreement with the statement of Hathaway *et al.*[16], which related the lowest *g* value of 2.04 to an elongated axial symmetry with all principal axes aligned parallel. Accordingly, the relation of g values in such symmetries was given by the expression:

$$G = \frac{g_{11} - 2}{g_1 - 2} = 4.0.$$

The application of the above relation using the present g values led

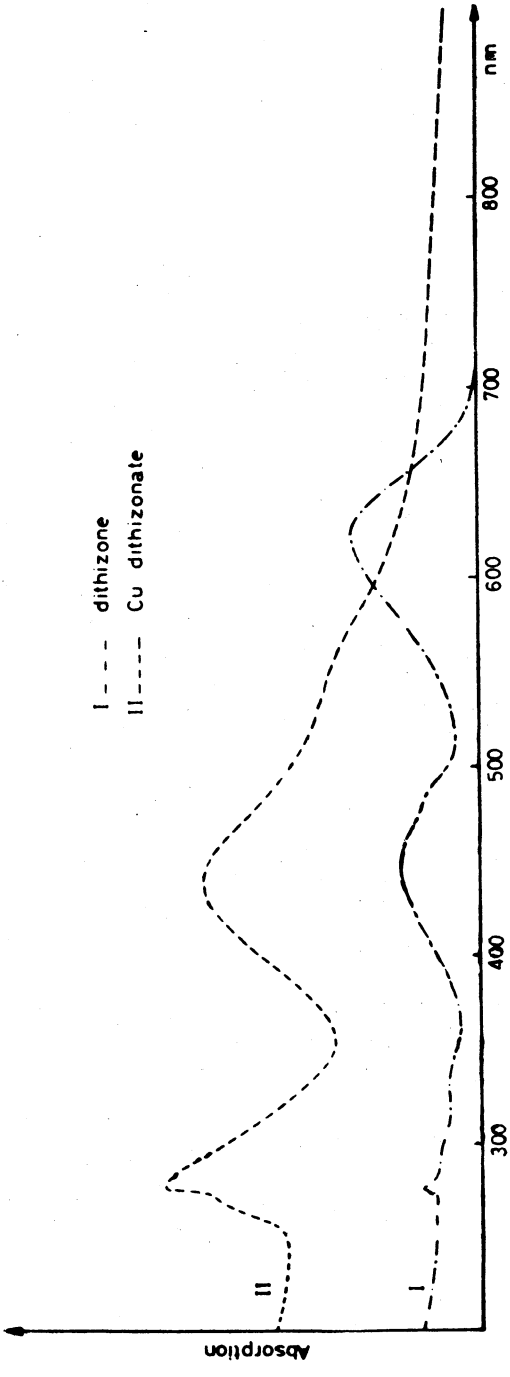


Fig. 2. Electronic absorption spectra of solutions of dithizone (I), and secondary copper (II) dithizonate complex (II) in benzene.

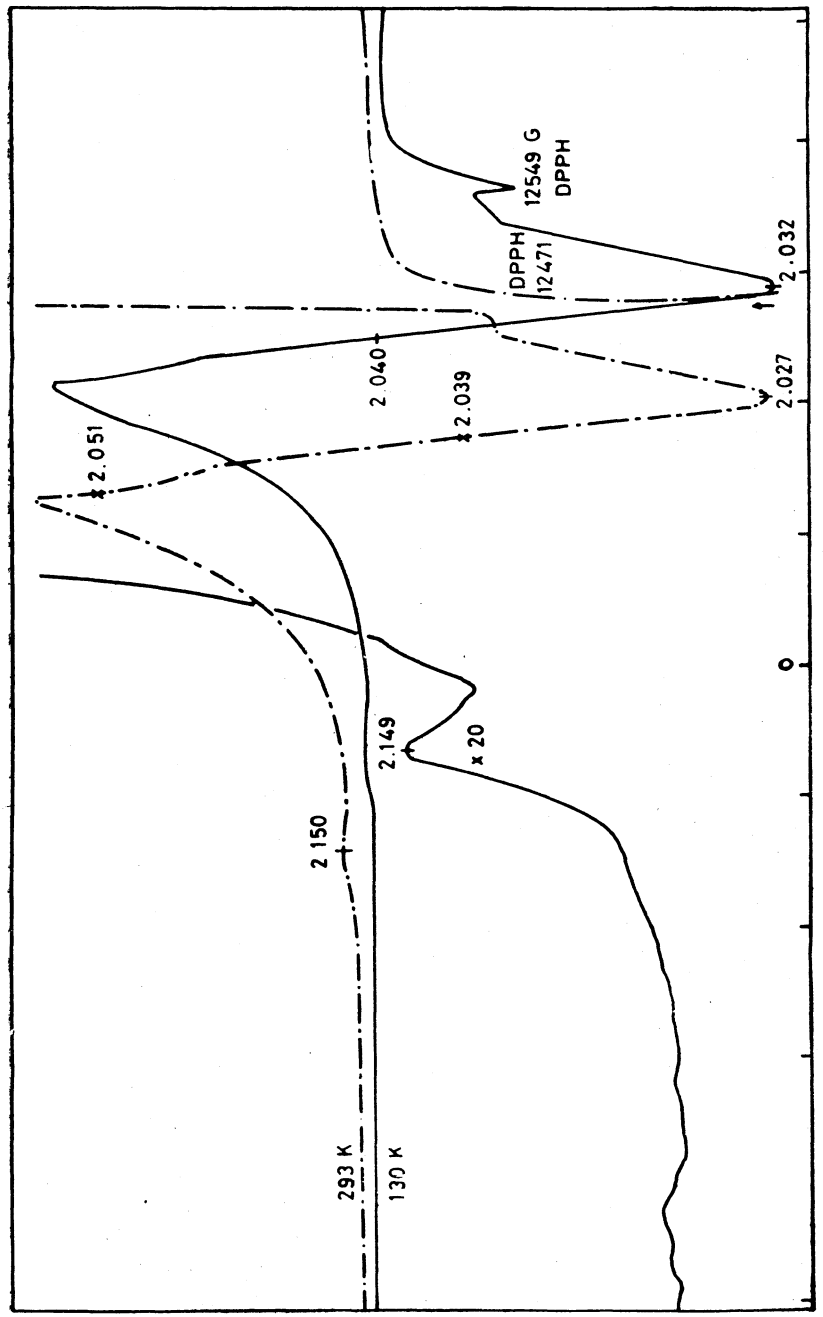


Fig. 3. EPR spectra of powder of secondary copper dithizonate complex at 130 (—) and 293 K (—.—.).

to a G value of 3.8, which indicates the presence of some exchange coupling and the misalignment of the principal axes is appreciable. The g_{11} values of 2.140–2.150 lie within the reported range of 2.1–2.2 for Cu-S and Cu-N bonds, respectively[17], confirming such mixed copper bonds in the present secondary copper dithizonate CuDz. Accordingly, the observed distortion of the equatorial plane around Cu(II) at the two working temperatures may be thus attributed to some variation of the ligand field strength of N and S atoms. Moreover, the presence of two differently bonded N atoms (2N of $-N=N-$ and $Ph-N-$) to Cu^{2+} as supported from IR spectrum may contribute to such distortion. It appears, however, that the proposed molecular structure is somewhat strained. It is now generally accepted that strained structures are less stable and their g values don't appreciably change if the strain is completely random[18]. Actually the unstability of secondary Cu(II) dithizonate in solution (in sense of colour change) is observed and also the magnitude of g values remained seemly unchanged (Fig. 3, curve 1 and 2). The covalent character of N and S mixed donors might exceed that of mixed N and O or only O-donors, since the group overlap integral between the copper $d_{x^2-y^2}$ orbital and the assumed sp^2 hybrid ligand σ orbital of oxygen and nitrogen is different ($S_{oxygen} = 0.076 < S_{nitrogen} = 0.093$). Accordingly, substitution of ligands around Cu^{2+} in the sequence:
$40 \rightarrow N_2O_4 \rightarrow N_3S$ would lead to an increase in covalency. Such conclusion could be further tested and estimated by calculating the covalency parameters K_{11} and K_1 with the assumption of D_{4h} symmetry and using the general equation:

$$\mu_{11}(\mu_1) = \frac{\lambda K_{11}^2(K_1^2)}{E} \text{ with } 8\mu_{11} = g_{11} - g_0 \text{ and } 2\mu_1 = g_1 - g_0 (\lambda = 830\ cm^{-1},$$

$E = 17540\ cm^{-1}$, $g_{11} = 2.150$, g_1 iso $= 2.039$ and $g_0 = 2$).

Actually the calculated values of $K_{11} = 0.63$ and $K_1 = 0.64$ are obviously lower by comparison with those obtained in some known Cu-coordinated compounds having nearly the same equatorial symmetry of D_{4h}(CuO_4 in Egyptian blue $K_{11} = 0.81$, $K_1 = 0.76$,[19] CuO_2N_2 in diphenylcarbazonate $K_{11} = 0.65$, $K_1 = 0.71$)[20].

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