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Spectroscopic Studies on Copper (II) Diphenylcarbazonate Complex†

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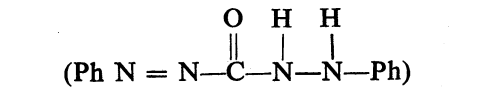
Copper diphenylcarbazonate complex was prepared by shaking very dilute copper sulphate solution (10^{-4} M) buffered at pH≃6 with stoichiometric quantity of purified diphenylcarbazone in benzene. The complex was separated from benzene solution by distillation under mild reduced pressure. Measurements of X-ray diffraction, IR, electronic and mass spectra of the ligand and its Cu(II) complex together with their elemental analysis were carried out. ESR spectrum of the complex ($g_{11} = 2.214$, $g_{x/y} = 2.06$ and $g_{y/x} = 2.042$) was also measured. Generally, the results of IR, electronic and mass spectra revealed distinct differences between ligand and Cu(II) complex which could be related to the chelation process. Moreover, the data achieved from the combined electronic and ESR spectra results of the complex suggested that Cu^{2+} ion is present in an elongated octahedral coordination with orth-rhombic component superimposed, where the bonding character in the equatorial plane is more covalent than that in the axial direction ($K_{11} = 0.65 < K_1 = 0.71$).

INTRODUCTION

A considerable work in literature has been done on many compounds related to formazan system[1–6]. Some relevant published papers could be cited where different studies such as infrared spectra M(II) 1,3,5-triarylformazan complexes[5] as well as EPR spectra of 1 : 1 Cu(II) complexes of 1,5-diphenylformazan, 1-(2-hydroxyphenyl)—3,5-diphenylformazan and 1-(2-carboxyphenyl)-3,5-diphenylformazan[6] were performed. The previous mentioned results of EPR spectra showed that these complexes in aqueous ethanol can add NH_3 to form a square planer complexes. However, the present ligand diphenylcarbazone, H_2DCO,



is one which is known to exist in keto-enolic form[7] has no substituted groups within 1,5-diphenyl rings, in addition to the presence of an active chromophoric C = O group. It appears, therefore, that the chelating ligand (H_2DCO) under investigation is different from the previously related studied ligands with respect to coordination centres. Although diphenylcarbazone has formed the subject of many articles and reviews which were devoted to spot testing and calorimetric reagents[8], and has

†IUPAC Nomenclature: Bis (1,5-diphenylcarbazonato-N,O)-Cu(II).

some non-analytical applications as a bactericidal material[9]. In addition, it appears alone or in admixture with some transition metals as a component in some commercial formulations and as a catalyst for hydroxylation of benzene, cyclohexene and cyclohexane[10]. The role of dipenylcarbazone in the previous mentioned application fields thought to be due to its ability to chelate various transition metal ions[10]. However, our knowledge on the coordination of such metal ions in these complexes is not much. Therefore, it is aimed in this article to throw some light on the fine geometrical symmetry of Cu(II) ion in Cu(II) diphenlycarbazonate complex.

EXPERIMENTAL

1. Purification of Reagents

(a) Benzene was made thiophene and methylthiophene free by refluxing with Na-K alloy[11].

(b) Sodium perchlorate-perchloric acid buffer solutions were treated before use with dithizone to remove interfering cations.[12]

(c) Diphenylcarbazone (H_2DCO) was purified by the removal of diphenylcarbazide from the commercial crude diphenylcarbazone[13]. The melting point of the resulting pure diphenylcarbazone (H_2DCO) was 119-121°C.

2. Preparation of Copper Diphenylcarbazonate Complex [$Cu(HDCO)_2$]

$Cu(HDCO)_2$ was prepared by shaking—for 10 minutes—one litre of 2.10^{-4}M solution of purified diphenylcarbazone in thiophene free benzene with one litre of 10^{-4}M aqueous solution of copper sulphate buffered at pH 6 with perchloric acid-sodium perchlorate buffer mixture, 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 40°C. The residual copper diphenylcarbazonate complex was washed thoroughly several times with water to remove unreacted copper sulphate followed by washing with benzene to remove unreacted ligand.

The ligand (H_2DCO) and the copper complex [$Cu(HDCO)_2$] were subjected to elemental analysis:

Ligand (Found: N = 23.07, C = 65.16 and H = 4.97%; Calcd: N = 23.42, C = 65.26 and H = 4.63%).

Copper complex (Found: N = 19.72, C = 58.53, H = 4.08 and Cu = 11.78%; Calcd: N = 20.67, C = 57.61, H = 4.09 and Cu = 11.2%).

Spectroscopic Measurements

IR spectra were recorded using a Perkin-Elmer 577 spectrophotometer

(KBr-disc method). All mass spectra were measured on Kratos MS 50 mass spectrometer provided with data system. Electronic spectra of solids (diffuse reflectance method) were recorded against MgO as a reference using an automatic Carl Zeiss DMR 21 spectrophotometer, whereas E 15-Varian spectrophotometer was used in measuring the EPR spectrum of the copper complex in Q-band ($\simeq$ 35 GHz) using DPPH as inner standard. X-ray Philips diffractometer was used for measuring the X-ray patterns for ligand (H_2DCO) and its primay copper complex $Cu(HDCO)_2$ using CuK radiation, = 1.5418 and Nickel filter.

RESULTS AND DISCUSSION

IR-spectra

The important infrared group frequencies of the ligand and the copper complex are assigned and given in Table 1. Apart from similar group frequencies in the two corresponding spectra (Fig. 1), the following observations could be pointed out:

TABLE 1
ASSIGNMENT OF SOME IMPORTANT
IR-FREQUENCIES (cm^{-1}) OF H_2DCO AND $Cu(HDCO)_2$

H_2DCO	$Cu(HDCO)_2$	Assignment
3380(w)	—	—NH, may be bonded or involved in keto-enolic transformation
—	3295(s)	NH stretching
3280(w)	—	NH hydrogen bonded
3190(m)	—	NH in NHCO
—	3050(m)	=CH stretching
1710(vs)	—	C=O stretching
1685(sh)	—	NHCO stretching
1600(s)	1600(s)	N=N or phenyl stretching
—	1590(s)	N=C stretching
—	1540(s)	NH bending
—	1380(vs)	=C—H bending in phenyl group
1305(m)	1305(s)	Ph-N modes
1120(s)	—	C=OH carbonyl group with some double bond character, which means the presence of some keto-enol tautomerization
—	1150(s)	C—O—Cu stretching
—	1135(sh)	
—	940(s)	Cu—legand, stretching
—	930(s)	
—	565–545(br)	C—O superimposed with C=C bending frequency
—	515(m)	Cu—ligand, stretching
—	440(m)	
—	335(s)	
—	235(w)	

br = broad, m = medium, sh = shoulder, s = strong, vs = very strong, w = weak.

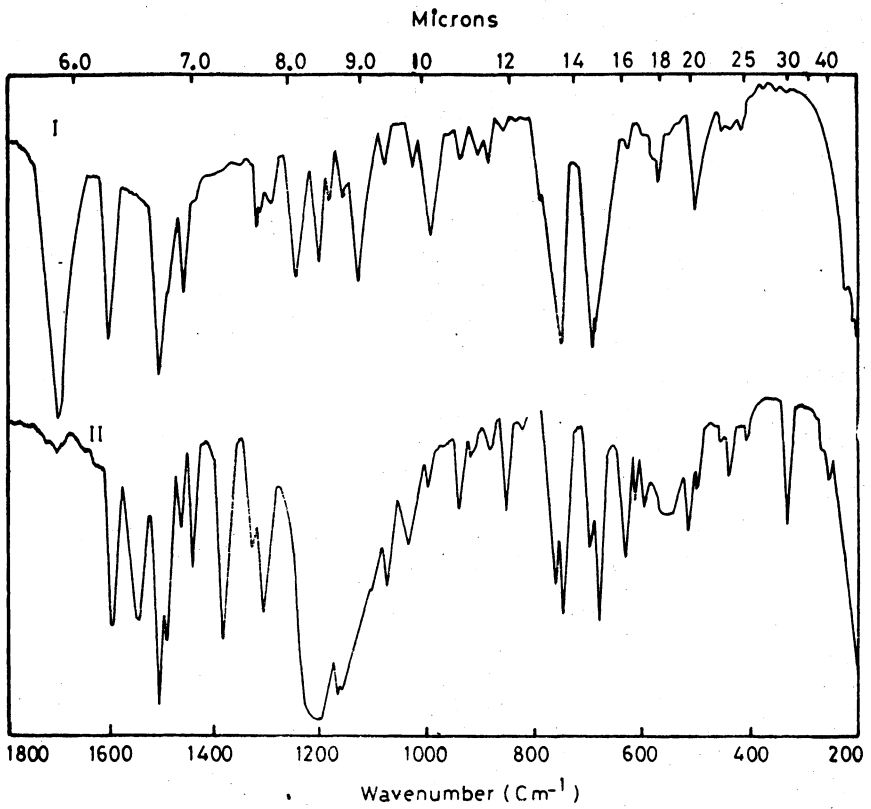


Fig. 1. IR-Vibrational Spectra of (I) Diphenylcarbazone and (II) Copper Diphenylcarbazonate Complex.

(i) Disappearance of some bands at 3380, 3190, 1710[14], 1685 and 1120 cm^{-1} from the spectrum of the pure ligand after the process of chelation.

(ii) Appearance of some new bands in the spectrum of the copper complex compared with that of pure ligand. These bands are found to be located at 3295, 1590, 1540, 1380 and in the range of 1105–235 cm^{-1} (Table 1 and Fig. 1).

(iii) Increase of intensity of some bands observed at 3050 ν(= CH) and 1305 ν(Ph-N) cm^{-1} in the spectrum of the complex in comparison with those of ligand.

(iv) Shift of NH stretching (3295.cm^{-1}) and phenyl group (1450–1500 cm^{-1}) bands towards longer wave numbers on complex formation.

It seems obviously that disappearance (i) and appearance (ii) of some characteristic bands related to the ligand before and after reaction with Cu(II) ions is an indication of a complex formation. Moreover, the increase of intensity of some bands (iii) as well as the shift of others (iv) in the spectrum of the copper complex could be due to a decrease of the degree

of electrons delecolization throughout the whole ligand residue as a result of complexation.

Mass Spectra

Generally the results of fragmentation of H_2DCO and $Cu(HDCO)_2$ as seen from Table 2 could be related to the following processes: (a) Cleavage of nitrogen—nitrogen, carbonyl carbon—nitrogen and nitrogen—phenyl bonds, (b) migration of proton to adjacent atoms or groups, (c) combination of Ph· with PhNH· and PhN· radicals to give Ph_2NH· and Ph_2N_2· respectively, and (d) rearrangement of diphenylamine (Ph_2NH·) into carbazole $(C_6H_4)_2$ NH·. The base peak of the ligand is found to be due to cleavage of phenyl-nitrogen bonds resulting in Ph· radicals, whereas that of the Cu(II) complex is due to a combination of Ph· with PhNH· radicals to give Ph_2NH·. Molecular Peak of the ligand (m/e = 169) was observed from its corresponding mass spectrum but that of copper complex gave no evidence of such peak. It is worthy to note however that imino-hydrogen atoms seem likely to migrate to phenyl groups and not to carbonyl carbon atoms in case of fragmentation process of ligand residue in the copper complex. Moreover, an increase of radicals combination giving Ph_2NH· and Ph_2N· together with an increase of diphenylamine rearrangement into carbazole is observed which may be due to catalytic effect of some copper complex and copper fragments (Table 2). Some additional fragments containing more than two nitrogen atoms, two or more phenyl groups and triphenylamine (m/e = 246) which undergoes rearrangement to N-phenylcarbazole (m/e = 244) were also characterized (Table 2). In case of ligand the abundance of fragments Ph_2NH· and $(C_6H_4)_2NH$· were found to be far less in comparison with its sulphur analogue (dithizone)[15] and with its copper complex (Table 2). On other hand, the present result concerning the absence of molecular peak of the copper complex together with its supposed catalytic effect is in a fairly agreement with the results obtained by Irving et al[15] on some transition metal dithizonates.

Electronic and ESR Spectra

(*a*) *Ligand*: Absorption spectrum of the ligand H_2DCO in carbon tetrachloride (Fig. 3, Ib) shows two absorption bands located at 21500 17860 cm^{-1} which are known to be due to keto and enol forms, respectively.[7] In addition, a very strong charge transfer band at 34720 cm^{-1} is observed. The effect of such charge transfer and on the two above mentioned characteristic absorption bands in case of reflectance spectrum of the ligand in solid state is obviously strong, so that their positions are changed and are difficult to be exactly estimated (Fig. 3, Ia).

(*b*) *Copper complex*: Since most of octahedrally coordinated Cu^{2+} ions

TABLE 2

SOME IMPORTANT FRAGMENTS OF MASS SPECTRA OF (H_2DCO) AND $Cu(HDCO)_2$

m/e	% abundance of H_2DCO fragments	% abundance of $Cu(HDCO)_2$ fragments	fragment	m/e	% abundance of H_2DCO fragments	% abundance of $Cu(HDCO)_2$ fragments	fragment
28	40.81	—	CO·	118	—	0.41	PhNHNC·
29.1	3.55	4.55	HCO.	119	—	11.20	PhNHNHC·
42.1	0.55	4·55	NCO·	121·5	—	0.42	NCOCuO·
43.1	1.56	25.93	HNCO·	122·5	—	0.54	NCOCuO.H·
44.3	0.95	3.36	H_2NCO·	128	—	1.32	$C_{10}H_8$·
56.0	1.06	—	NNCO·	134	28.97	3.80	PhNHNCO
57.1	0.46	1.63	HNNCO·	135	3·23	0.45	PhNHNHCO.
58.1	0.89	0.30	HNNHCO·	166	—	6.19	Ph–N–Ph
77.0	100.0	70.09	Ph·	167	0·61	26.34	Carbazole·
78.0	12.61	23.10	PhH·	168	2.29	43.05	Ph_2N·
82.5	—	0.81	HCuOH·	169	0.81	100.0	Ph_2NH·
83.5	—	4.02	H_2CuOH^+	169·5	—	0.53	PhNHNCu·
84.5	—	5.08	$C_4H_8CNCu^+$	170	—	12.79	Ph_2NH_2·
91.1	2.97	5.73	PhN·	180	—	1.2	Ph_2NH_3:
92.0	90.64	10.91	PhNH·	181	—	1.46	PhN_2CNPh·
93.1	17.74	31.27	$PhNH_2$·	210	—	3.05	PhN_4Ph·
105.1	15.81	22.67	PhNN·	240	8.4	1.32	H_2DCO·
106.1	5.18	4.10	PhNHN:	244	—	2.77	PC·*
107	44.33	4.39	PhNHNH·	245	—	17.86	Ph_3N·
108	4.24	1.05	$PhNHNH_2$·	246	—	2.91	Ph_3NH·
117	—	0.40	PhNNC.	260	—	2.28	Ph_2N_2Ph·

*PC = Phenylcarbazole.

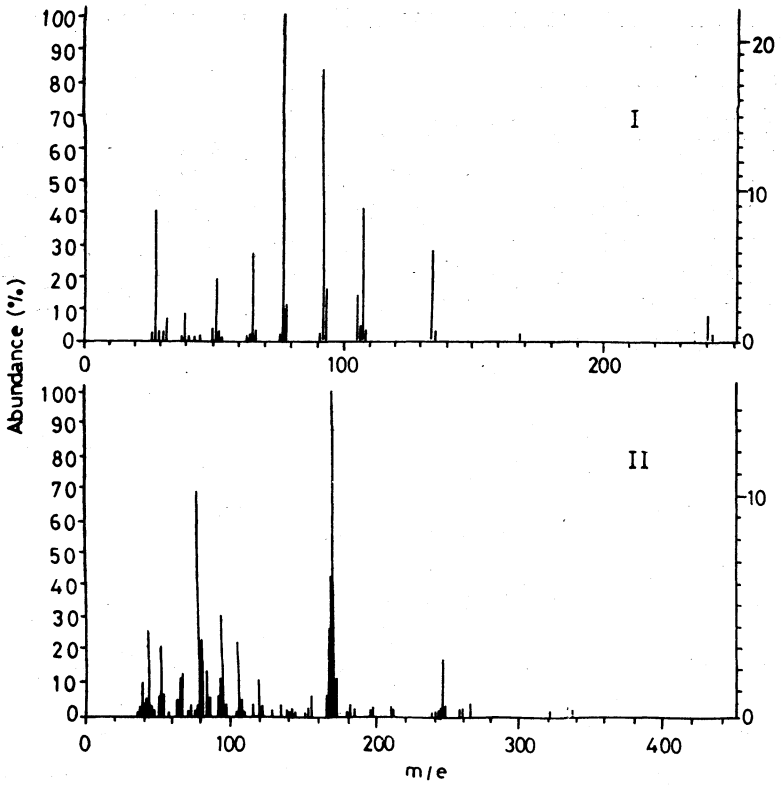


Fig. 2. Mass spectra of (I) Diphenylcarbazone and (II) Copper Diphenylcarbazonate Complex.

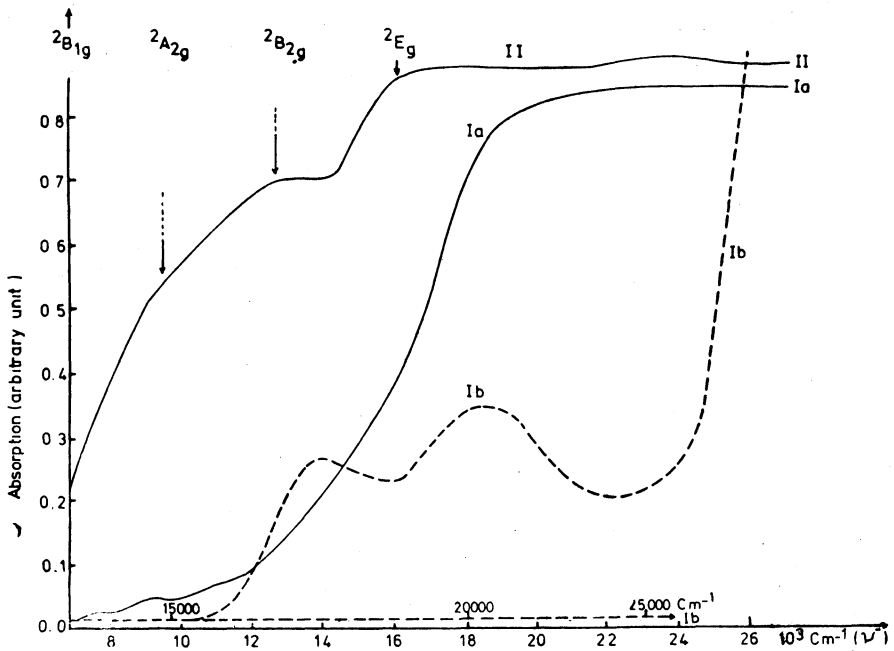


Fig. 3. Electronic Absorption Spectra of Diphenylcarbazone(I), *a*-solid, *b*-in Carbontetrachloride Solution and Solid Copper Diphenylcarbazonate Complex (II).

in different compounds are usually found to be always distorted[16] elongated or compressed D_{4h} symmetry one would thus expect a splitting of the low doubly ^2E_g and high triply $^2T_{2g}$ degenerated energy levels of Cu^{2+} -ions in non distorted octahedra into $^2B_{1g} + {}^2A_{1g}$ and $^2B_{2g} + {}^2E_g$, respectively[17]. However, the sequence of such energy levels is different whether the case is of elongation or compression nature. Assuming an elongated octahedron around Cu^{2+} ions in copper diphenylcarbazonate complex, the observed three d-d bands of the electronic spectrum (Fig. 3, II) could be assigned to the transitions:

$$\text{I} - {}^2B_{1g} \rightarrow {}^2A_{1g} \quad (9800\ cm^{-1})$$
$$\text{II} - {}^2B_{1g} \rightarrow {}^2B_{2g} \quad (13100\ cm^{-1})$$
$$\text{III} - {}^2B_{1g} \rightarrow {}^2E_g \quad (16400\ cm^{-1})$$

In addition, a weak broad charge transfer band centered at about 24000 cm^{-1} is observed which tails off into the blue end of visible spectrum causing the complex to appear brown.

On the otherhand, the ESR spectrum (Fig. 4) illustrates two g values, where the low field parallel transition $g_{11} = 2.214$ and the high field perpendicular one $g_1 = 2.051$ which show a slight resolution into $g_{x/y} = 2.042$ and $g_{y/x} = 2.06$ [where $g_1 = \frac{1}{2}(g_x + g_y)$] probably due to a small o-rhombic component superimposed. This may indicate that in the complex nitrogens and oxygens in the equatorial plane provide a slightly different ligand field strength. The value of g_{11} obtained lies within the range of 2.2-2.3 for Cu-N mixed Cu-N, and Cu-O bonds as reported earlier.[18] Generally, the trend of the obtained g components $g_{11} > g_1 > 2$

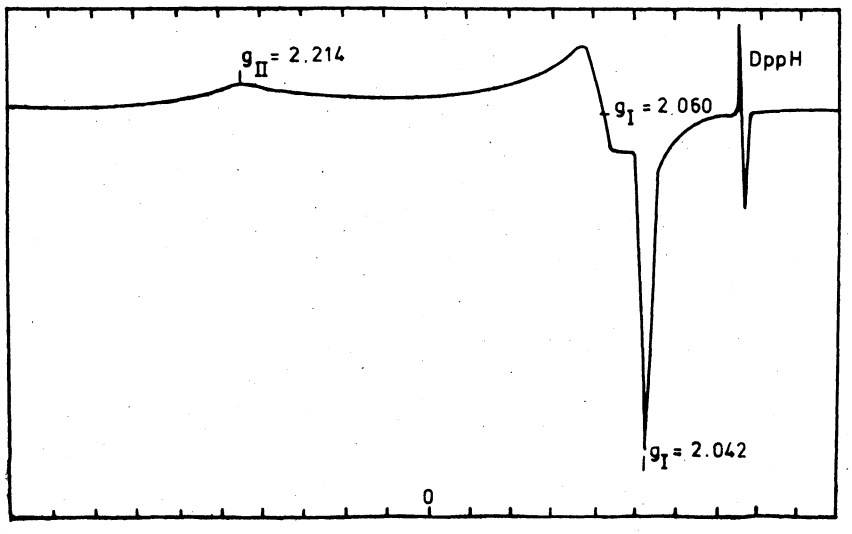
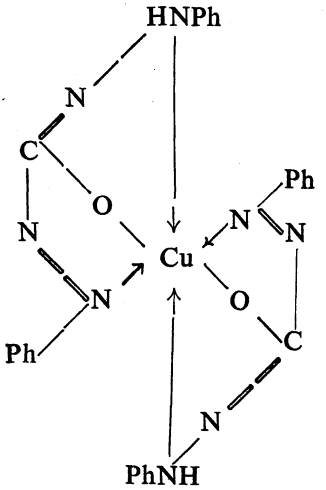


Fig. 4. ESR Spectrum of Solid Copper Diphenylcarbazonate Complex at 293°K.

is in agreement with $^2B_{1g}$ ground state of Cu(II) in an elongated axial symmetry. Since the value of the lowest *g*-factor (mean $g_1 = 2.051$) agrees with those already observed in similar Cu(II) axial spectra[19,20]. Accordingly environment of 2 O- and 2 N-atoms in the equatorial plan at a probably slightly different bond lengths, whereas the two nitrogen of imino groups of two diphenylhydrazone ligands approach the copper at a large distance completing the distorted octahedron. The structural formula of the $Cu(HDCO)_2$ complex may be thus given as:



The relation $\frac{g_{11} - 2}{g_1 - 2} = G \simeq 4$[16] holds for present result indicating that Cu(II) ions probably occupy crystallographically equivalent sites[20] without appreciable exchange coupling. Moreover calculations of orbital reduction factors K_{11} and K_1 by applying the expression valid for the symmetry of tetragonally elongated octahedra give the values,

$$K_{11} = \sqrt{\frac{(g_{11}-2)\cdot 13100}{8\lambda_0}} = 0.65 \text{ and } K_1 = \sqrt{\frac{(g_1 - 2)\cdot 16400}{2\lambda_0}} = 0.71$$

which suggests that bonding in equatorial plane in the studied $Cu(HDCO)_2$ complex is more covalent than that in axial direction ($K_{11} < K_1$). The same phenomenon of covalency character ($\alpha = 0.79$–84)[6] was observed in some 1 : 1 Cu(II) complexes of ligands based on formazan system. This conclusion could also be supported by the obtained value of $g_{11} = 2.214$ (< 2.3) which is taken as a function of more covalency characer (18).

As far as it is known to the authors, the diffraction patterns of diphenylcarbazone and its primary copper complex were not previously done. Therefore we include their diffractograms herewith (Fig. 5, Tables 3a & b). Some differences between the ligand and the complex with respect to inter-

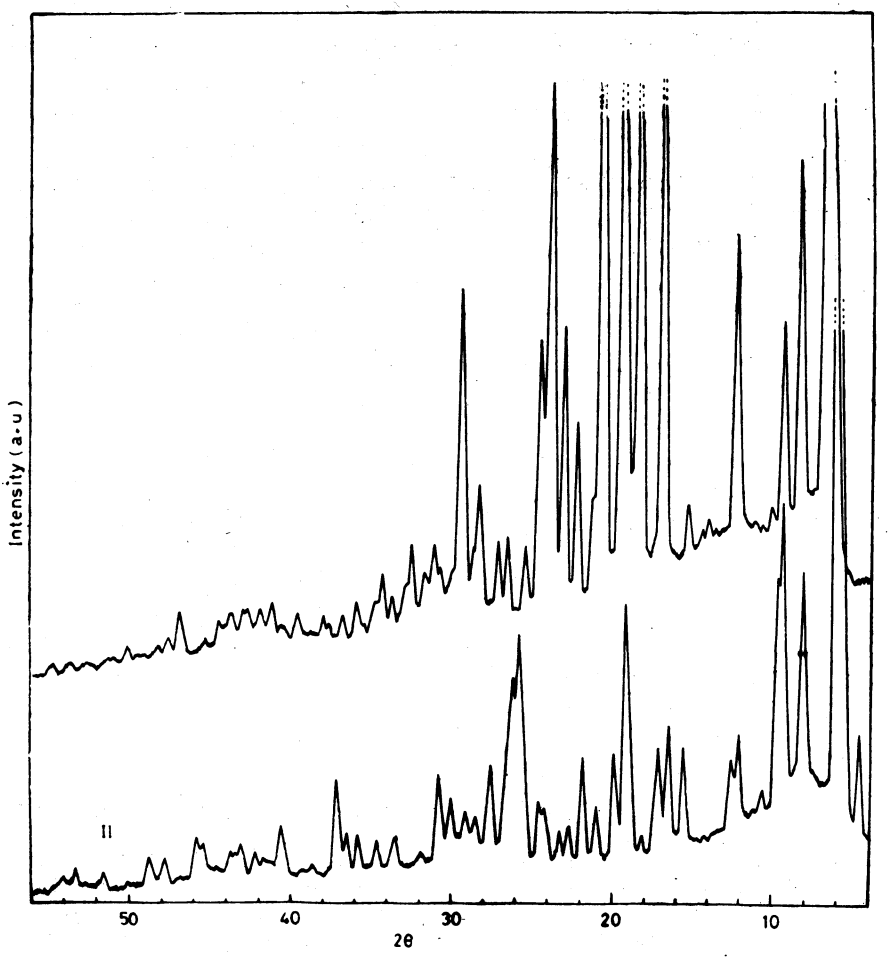


Fig. 5. X-ray Diffraction Pattern of (I) Diphenylcarbazone and (II) Copper Diphenylcarbazonate Complex Taken with an X-ray Diffractmeter, Uaing CuK Radiation and Nickel Filter.

TABLE 3-a

POWDER X-RAY DIFFRACTION PATTERN OF DIPHENYLCARBAZONE

dA°	I	dA°	I	dA°	I
12.8	100.00	3.720	55.56	2.435	1.85
11.47	39.51	3.617	25.31	2.383	1.39
9.21	27.62	3.477	6.17	2.365	2.01
8.54	6.48	3.336	7.25	2.312	< 1
8.12	5.86	3.276	6.79	2.268	2.78
7.89	6.48	3.140	12.35	2.214	1.85
7.07	32.72	3.100	6.48	2.189	4.01

TABLE 3-a (*Contd.*)

dA°	I	dA′	I	dA°	I
6.65	5.86	3.015	30.86	2.149	3.40
6.45	5.86	2.957	4.63	2.111	3.70
6.27	6.64	2.901	5.09	2.101	3.70
6.06	5.86	2.864	7.41	2.065	3.55
5.639	8.49	2.816	4.94	2.034	2.93
5.196	64.81	2.744	7.72	1.999	1.70
4.792	72.53	2.712	3.36	1.931	4.17
4.548	74.38	2.652	3.09	1.906	1.85
4.267	87.96	2.605	4.94	1.882	1.23
4.168	9.57	2.568	2.78	1.816	1.54
3.966	16.97	2.526	< 1	1.785	< 1
3.847	26.08	2.493	3.09	1.735	< 1
				1.702	< 1
				1.676	< 1

The relative intensities, referred to the strongest line as 100 are given under I. The intensities are derived from measurements of peak height above background.

TABLE 3-b

POWDER X-RAY DIFFRACTION PATTERN OF COPPER DIPHENYLCARBAZONATE

dA°	I	dA°	I	dA°	I
18.8	12.33	3.914	4.71	2.324	2.69
15.23	100.00	3.831	4.26	2.284	2.02
10.77	34.98	3.767	1.79	2.220	8.07
9.30	46.19	3.660	7.17	2.159	3.59
9.11	34.53	3.617	8.52	2.134	4.48
8.26	6.73	3.444	31.39	2.097	5.61
7.96	4.48	3.386	25.56	2.078	4.48
7.30	14.8	3.230	13.90	2.065	4.48
7.01	11.66	3.124	7.17	2.030	2.69
6.18	1.79	3.066	8.07	1.991	5.58
5.676	13.90	2.966	9.87	1.979	6.95
5.368	17.04	2.901	12.45	1.935	2.02
5.180	14.35	2.795	3.14	1.901	4.48
4.870	2.24	2.672	5.38	1.864	4.48
4.643	34.09	2.576	4.93	1.816	1.35
4.458	13.90	2.499	5.83	1.769	2.70
4.247	7.17	2.453	6.73	1.717	4.04
4.078	14.13	2.415	14.13	1.691	2.69

The relative intensities, referred to the strongest line as 100 are given under I. The intensities were derived from measurements of peak height above background.

planar spacings (dA°) as well as relative intensities of diffracted lines were observed, which could be due to a differently crystalline structure. An indexing of the two systems is aimed to be proceeded in future.

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