

## Aromatic Diamine Complexes Part III, Copper (II) Complexes With o-Phenylenediamine, 1,8-Diaminonaphthalene, and 2,2'-Diaminobiphenyl.

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(Received 5th April, 1980, Revised 9th March 1981)

**Summary:** Complexes of aromatic diamines with copper (II) salts have been prepared and characterized by infra-red, electronic spectral analysis and magnetic measurements. The complexes are of the type  $\text{CuLX}_2$ ; where L=o-phenylenediamine and  $\text{X}=\text{Cl}^-$  or  $\text{Br}^-$ , having a polymeric octahedral structure; and  $\text{CuL}_2\text{X}_2$ ; where L=o-phenylenediamine, 1,8-diaminonaphthalene or 2,2'-diaminobiphenyl, and  $\text{X}=\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  and  $\frac{1}{2}\text{SO}_4^{2-}$  which are shown to be of a distorted octahedral nature.

### Introduction

Aromatic diamine complexes containing two and three molecules of the diamine, o-phenylenediamine; 1,8-diaminonaphthalene and 2,2'-diaminobiphenyl per metal ion (M=Nickel (II)<sup>(2)</sup>, cobalt (II)<sup>(3)</sup>) have been reported previously. The complexes characterized by infra-red, electronic spectral measurements and magnetic properties have been shown to have tetragonal ( $D_4h$ ) symmetry around the metal atom. Previous reports of copper (II) complexes with aromatic diamines are very scarce. Hieber and his coworkers<sup>(4)</sup> have reported the complexes  $\text{Cu}(\text{NO}_3)_2 \cdot \text{opda}_2$  and  $\text{CuSO}_4 \cdot \text{opda}_2$  which appeared to contain bidentate diamine. Duff<sup>(5)</sup> has also reported the preparation and spectroscopic data of some o-phenylenediamine copper (II) complexes. From these studies, it is inferred that the (1:1) complexes ( $\text{CuLX}_2$ ,  $\text{X}=\text{Cl}^-$ ,  $\text{Br}^-$ ) involve a planar halide environment for Cu(II), whereas for the (1:2) complexes ( $\text{CuL}_2\text{X}_2$ ,  $\text{X}=\text{NO}_3^-$ ,  $\text{ClO}_4^-$  and  $\text{SO}_4^{2-}$ ) a tetragonal environment around the copper (II) atom exists. The only available reference in the literature about the metal complexes of 1,8-diaminonaphthalene are by Poni<sup>(6)</sup> and Pfeiffer et al<sup>(7)</sup> who have reported a number of first two transition metal compounds including that of Copper (II). Schmidt et al<sup>(8)</sup> from their studies on the infrared spectra of the addition compounds with diaminobiphenyls (ortho, meta, para) proposed a seven membered ring structure for  $\text{Cu}(\text{diaminobiphenyl})_2\text{Cl}_2$  and analogous metal complexes of cobalt, nickel, zinc and cadmium. Copper (II) complexes of 2,2'-diaminobiphenyl

containing acetate as the anion have also been reported by Onaka et al<sup>(3)</sup>. From the infra red, diffuse reflectance spectra and the magnetic properties, the copper(II) ion in the complex,  $[\text{Cu}(2,2'\text{-diaminobiphenyl})(\text{CH}_3\text{-COO})_2]$  is shown to be coordinated to the two nitrogen atoms of the diamine and two oxygen atoms of the acetate groups. A square planar cis structure has thus been proposed, since the two stretching frequencies were observed at 393 and 385  $\text{cm}^{-1}$  in the far infra red spectra,

In view of the generality of tetragonal structures for the nickel (II)<sup>(2)</sup> and cobalt (II)<sup>(3)</sup> complexes with the aromatic diamines and the lack of information on copper (II) complexes of similar structure, the investigation reported here was carried out.

In this paper we report the synthesis and characterization of copper (II) complexes with the three aromatic diamines, o-phenylenediamine (opda), 1,8-diaminonaphthalene (dan) and 2,2'-diaminobiphenyl (dabp), their structures having been deduced by infrared, electronic spectral measurements and magnetic properties.

### Experimental

O-Phenylenediamine (opda), 1,8-diaminonaphthalene (dan) and 2,2'-diaminobiphenyl (dabp) were obtained and purified as previously described.<sup>(2)</sup> Copper perchlorate was prepared from copper carbonate and perchloric acid and recrystallized from ethanol. Attempts to

prepare copper iodide and the thiocyanate analogue in situ were unsuccessful. The following general methods for the preparation of the complexes were employed:

1.  $\text{CuLX}_2$  Complexes: (L=opda, X=Cl<sup>-</sup>, Br<sup>-</sup>): Solvents used for the preparation of these complexes were deoxygenated by passing oxygen free nitrogen through them before use. Stoichiometric amounts (1:1) of the diamine (opda) in ethanol (20 mls) and the anhydrous halide in ethanol (20 mls) were mixed together. The complexes are filtered off, washed with ethanol and light petroleum (30-40°C) and dried in vacuum.

$\text{CuL}_2\text{X}_2$  Complexes: (L = opda, dan, dabp; X = Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>) warm ethanolic solution of the hydrated copper salt (0.001 moles in 25 mls) was added slowly with stirring to a warm solution of the stoichiometric amount of the diamine (0.003) moles in 25 mls of ethanol. The complexes precipitated out immediately or crystallized out on cooling overnight. The complexes were removed by filtration, washed with alcohol and dried under vacuum. Modification to the general methods described above are as follows:

Diperchloratobisorthophenylenediamine copper (II).  $[\text{Cu}(\text{opda})_2] (\text{ClO}_4)_2$ : An ethanolic solution of cupric perchlorate tetrahydrate (2.67 gms) was added to a solution of o-phenylenediamine in ethylacetate. The purple coloured compound obtained was filtered off, washed with ethanol and light petroleum (30-40°C) and dried under vacuum. Yield. 65%.

Diaquobisorthophenylenediamine copper (II) sulphate.  $[\text{Cu}(\text{opda})_2 (\text{H}_2\text{O})_2] \text{SO}_4$ : An aqueous ethanolic solution of cupric sulphate pentahydrate (0.832 gms) was added to a warm solution of the diamine in ethanol. The violet coloured compound was filtered off, washed with ethanol and ether and dried under vacuum. Yield 82%.

Bis (1,8 diaminonaphthlene) copper (II) nitrate.  $[\text{Cu}(\text{dan})_2 (\text{NO}_3)_2]$ : An aqueous ethanolic solution of copper nitrate hexahydrate (2 gms) was added to an ethanolic solution of the (dan). Greyish black crystals separated on scratching the sides of the beaker with a glass rod, which were washed with ethanol after filtration and dried under vacuum. Yield = 27%.

Diperchloratobis (2,2' diaminobiphenyl) copper(II).  $[\text{Cu}(\text{dabp})_2] (\text{ClO}_4)_2$ : A solution of copper perchlorate hexahydrate (0.84 gms) in absolute alcohol was added to a solution of the diamine (dabp) in absolute alcohol. The complex was precipitated from the solution by the addition of anhydrous ether. The complex was filtered by

suction, washed with ether and dried under vacuum. Yield 80%.

Diaquobis (2,2' diaminobiphenyl) copper (II) sulphate was prepared in a similar manner.

### Physical Measurements

Infrared spectra from 4000-400  $\text{cm}^{-1}$  were measured on a Perkin Elmer 337 and 125 spectrophotometers and from 400-40  $\text{cm}^{-1}$  on an R.I.I.C., F.S. 620 interferometer and computed on an F.T.C. 100 computer to a limiting resolution of 2.5  $\text{cm}^{-1}$ . The spectra were calibrated against water vapour. Electronic spectra were run on a Perkin Elmer 450 spectrophotometer. Magnetic moments at room temperature were obtained using a Guoy balance. Diamagnetic corrections based on Pascals constants given by Lewis<sup>10</sup> were used. Microanalysis for carbon, hydrogen and nitrogen were performed by A. Bernhardt Microanalytical Laboratories, W. Germany.

### Results and Discussion

The complexes obtained with the three diamines, o-phenylenediamine (opda) 1,8 diaminonaphthlene (dan), and 2,2' diaminobiphenyl (dabp) are listed in Table I, together with the ratio of copper ion to, ligand used in their formation and the analytical data. The reaction of o-phenylenediamine with copper chloride and the corresponding bromide results in the isolation of (1:1) complexes i.e.,  $(\text{Cu}(\text{opda})\text{X}_2)$ ; where X=Cl<sup>-</sup> or Br<sup>-</sup> and; (1:2) complexes, i.e.,  $(\text{Cu}(\text{opda})_2\text{X}_2)$ ; where X=Cl<sup>-</sup> or Br<sup>-</sup> depending upon the ratio of ligand to copper used. The (1:1) complexes obtained have been assigned polymeric octahedral structures involving a planar halide environment for the copper (II) ion, (bridging halide groups) with the ligand molecules along the polar axis<sup>5</sup> These will not be discussed any further here.

For the bisdiamine complexes, the characteristic infra red absorption bands for both free and coordinated ligands and anions where applicable are listed in Table II. It can readily be seen that for the three ligands coordination to copper (II) ion results in lowering of bands assigned to  $\nu$  (NH),  $\delta$  (NH<sub>2</sub>) and  $\nu$  (CN) frequencies in all cases. Similar shifts were observed for the nickel (II)<sup>2</sup> and cobalt (II)<sup>3</sup> complexes containing these ligands<sup>2,3</sup> and it is concluded that in the copper (II) complexes reported here, all three diamines are behaving as bidentate ligands.

Table 1. Analytical and Magnetic Data for the Complexes.

Compound	Ratio Cu-L used	Calculated %			Found %			$\chi_{\text{corr}} \times 10^6$ $\chi_{\text{m}}$	$10^6 \mu_{\text{eff}}$ $T^{\circ}\text{K}$	B.M.
		C	H	N	C	H	N			
Cu(opda)Cl <sub>2</sub>	1=1	29.70	3.30	11.60	30.45	3.40	11.09	1484	294	1.84
Cu(opda)Br <sub>2</sub>	"	21.70	2.45	8.50	22.29	2.50	8.88	1546	294	1.91
Cu(opda) <sub>2</sub> Cl <sub>2</sub>	1=3	41.14	4.56	16.00	40.89	4.75	15.64	1691	293	1.98
Cu(opda) <sub>2</sub> Br <sub>2</sub>	"	32.80	3.64	12.75	32.34	3.67	12.61	1472	293	1.87
Cu(opda) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	"	35.68	3.96	20.81	35.73	3.91	20.83	1598	292	1.93
Cu(opda) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	*	30.08	3.48	11.88	30.08	3.34	11.70	1795	292	2.01
Cu(opda) <sub>2</sub> SO <sub>4</sub> ·2H <sub>2</sub> O	1=3	35.20	4.80	13.60	36.42	4.49	13.64	1770	290	1.98
Cu(opda) <sub>2</sub> SO <sub>4</sub>	**	38.10	4.80	14.90	37.80	4.65	14.70	1685	292	1.96
Cu(dan) <sub>2</sub> Cl <sub>2</sub>	1=3	53.27	4.43	12.42	53.33	4.52	12.49	1408	293	1.84
Cu(dan) <sub>2</sub> Br <sub>2</sub>	"	44.47	3.70	10.37	44.55	3.82	10.28	1612	294	1.93
Cu(dan) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	"	47.65	3.97	16.68	47.73	4.50	16.51	1712	293	1.98
Cu(dan) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	"	41.48	3.45	9.67	41.58	4.50	8.70	1823	293	2.07
Cu(dan) <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	"	48.68	4.46	11.36	48.93	4.74	11.50	1435	293	1.84
Cu(dabp) <sub>2</sub> Cl <sub>2</sub>	"	57.30	4.77	11.14	57.03	5.19	10.88	2063	291	1.87
Cu(dabp) <sub>2</sub> Br <sub>2</sub>	"	48.65	4.50	9.46	48.56	4.20	9.55	1927	291	2.03
Cu(dabp) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	"	51.83	4.31	15.11	51.70	4.45	15.31	1745	293	1.99
Cu(dabp) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	"	45.71	4.80	8.88	46.75	4.57	8.31	1803	292	2.04
Cu(dabp) <sub>2</sub> SO <sub>4</sub> ·2H <sub>2</sub> O	"	51.15	4.97	9.94	51.01	4.63	9.87	1687	292	1.98

The use of infra red data for determining whether the polyanions present in a complex are coordinated to the transition metal used, or, are present as free ions is well established in the case of nitrate<sup>11</sup>, perchlorate<sup>12</sup> and sulphate<sup>13</sup> ions. Coordination lowers the original symmetry of the free ion and results in the splitting of the originally degenerate modes, the previously forbidden i.r., modes thus becoming allowed. Thus in tetrahedral polyanions, monodentate coordination results in a lowering of symmetry ( $T_d-C_{3v}$ ), the originally triply degenerate modes,  $\nu_3$ , and  $\nu_4$ , of the free ion, each split in to a non-degenerate and a degenerate mode and the previously forbidden i.r., modes  $\nu_1$  and  $\nu_2$  of the free ion become i.r., active.

The anion infra red bands of the nitrate complexes are very similar to those observed in the related complexes containing unidentate nitrate groups<sup>14</sup>. Strong bands observed in the region 1440-1410, 1330-1305, 1050 and 1010  $\text{cm}^{-1}$  respectively thus indicate the presence of unidentate nitrate ion. Hathaway and Underhill<sup>12</sup> from their studies on the infrared spectra of ionic perchlorates and perchlorato groups have shown that as the perchlorate ion becomes involved in covalent bond-

ing, its symmetry is lowered from  $T_d$  to  $C_{3v}$  or  $C_{2v}$  depending on whether one or two of its oxygen atoms are involved in bonding. Each of the two infra-red active bands in  $T_d$  symmetry  $\nu_3$  and  $\nu_4$  which occur at 1100  $\text{cm}^{-1}$  (antisymmetric stretch) and at 625  $\text{cm}^{-1}$  (antisymmetric bend) are split into two components in  $C_{3v}$  symmetry and into three components in  $C_{2v}$  symmetry, thus making it possible to distinguish between the type of perchlorate groups present. In all the complexes studied during this work, where the perchlorate was coordinated, splitting occurred into two bands only, ( $\nu_3 = 1110$  and  $1065 \text{ cm}^{-1}$ ) and ( $\nu_4 = 630$  and  $625 \text{ cm}^{-1}$ ) indicating that the perchlorate group was coordinating through only one oxygen.

The effect on the infra-red spectrum of the sulphate ion (having a  $T_d$  symmetry) on coordination both via one and two oxygen atoms has been studied by Nakamoto et al<sup>13</sup> and Baldwin<sup>15</sup>. It is believed that the strong bands observed at 1220, 1176, 1075 and 1050  $\text{cm}^{-1}$  together with the band of medium intensity at 993  $\text{cm}^{-1}$  can be assigned to a sulphate group of  $C_{3v}$  symmetry. The absence of a strong band due to sulphate ion close to 1220  $\text{cm}^{-1}$ , however, suggests that this anion

Table 2. Characteristic Infra red Absorption Bands 4000-40  $\text{cm}^{-1}$ .

Compound	$\nu(\text{N-H})$	$\delta(\text{NH}_2)$	(CN)	Anion X	$\nu(\text{Cu-X})$	$\delta(\text{Cu-X})$	$\nu(\text{Cu-N}_{\text{lig}})$
opda	3380,3360	1620	1270	—	—	—	—
	3280,3180						
$\text{Cu}(\text{opda})\text{Cl}_2$	3260,3230	1605	1250	—	316,214	—	292.
	3200,3160						
	3080.						
$\text{Cu}(\text{opda})\text{Br}_2$	3280,3240	1600	1240	—	272,180	—	284.
	3200,3120						
	3090,3060						
$\text{Cu}(\text{opda})_2\text{Cl}_2$	3270,3240	1600	1245	—	312	108	288.
	3160,3090						
	3060						
$\text{Cu}(\text{opda})_2\text{Br}_2$	3300,3250	1600	1230	—	260	92	284.
	3140,3080						
$\text{Cu}(\text{opda})_2(\text{NO}_3)_2$	3290,3180	1600	1245	1425,1310	184	—	296.
	3130,3110			1015.			
$\text{Cu}(\text{opda})_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$	3220,3200	1610	1240	35= $\text{H}_2\text{O}$	—	—	284.
	3250,3230			1120,1050			
	3110.			(Broad band)			
$\text{Cu}(\text{opda})_2\text{SO}_4$	3220,3290	1610	1235	1135,1080	—	—	—
	3270,3240						
	3200,3160						
dan	3410,3380	1620	1260	—	—	—	—
	3330,3300						
$\text{Cu}(\text{dan})_2\text{Cl}_2$	3240,3180	1620	1230	—	252	128	326 <sup>sh</sup>
	3120,3060						
$\text{Cu}(\text{dan})_2\text{Br}_2$	3230,3200	1615	1225	—	116	64	320 <sup>sh</sup>
	3160,3130						
	3110.						
$\text{Cu}(\text{dan})_2(\text{NO}_3)_2$	3280,3240	1610	1225	1420,1320	104	—	308
	3170,3120						
$\text{Cu}(\text{dan})_2(\text{ClO}_4)_2$	3300,3240	1610	1230	1150,1070	—	—	296.
	3170,3120						
$\text{Cu}_9\text{dan}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	3280,3230	1605	1220	3480= $\text{H}_2\text{O}$	—	—	328 <sup>sh</sup>
	3170,3140			1130-1070			
				(Broad band)			
dabp	3400,3380	1630	1230	—	—	—	—
$\text{Cu}(\text{dabp})$	3270,3170						
$\text{Cu}(\text{dabp})_2\text{Cl}_2$	3370,3300	1610	1230	—	280	192	320 <sup>sh</sup>
	3280,3260						
	3080.						
$\text{Cu}(\text{dapb})_2\text{Br}_2$	3350,3180	1605	1220	—	142	88	316 <sup>sh</sup>
	3150,3100						
$\text{Cu}(\text{dapb})_2(\text{NO}_3)_2$	3300,3280	1610	1220	1435,1310	164	—	312
	3200,3160						
	3080.						
$\text{Cu}(\text{dapb})_2(\text{ClO}_4)_2$	3300,3240	1600	—	1090-1039	—	—	318 <sup>sh</sup>
	3126.						
$\text{Cu}(\text{dapb})_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$	3300,3260	1600	1225	3400= $\text{H}_2\text{O}$	—	—	316.
	3240,3160			1110-1040			
	3080			(Broad band).			

sh = sou sh = shoulder on ligand absorption.

is present as a bridging rather than a chelating group<sup>16</sup> in Bis *o*-Phenylenediamine copper (II) sulphate. The aquo complexes of copper sulphate on the other hand show a broad infra red band between 1070 and 1150  $\text{cm}^{-1}$  which together with the characteristic broad band around 3560  $\text{cm}^{-1}$  and a strong band at 838  $\text{cm}^{-1}$  indicates the presence of coordinated water<sup>17</sup> and ionic sulphate.

Table II also records the metal halogen, metal nitrogen (metal-ligand) stretching frequencies and other bands of copper (II) complexes in the region 400-400  $\text{cm}^{-1}$ . Numerous references to the metal-halogen vibrations of the bridging halide atoms in copper (II) halide complexes are available in the literature. Thus the complex  $\text{Cu}(\text{pyridine})_2\text{Cl}_2$  is polymeric in the solid state and its structure is composed of distorted octahedra connected by chlorine atoms<sup>18</sup>. In each octahedron there are two long (3.05 Å) and two short (2.28 Å) copper chloride bonds. In the far infra red spectrum of this compound absorption due to copper chlorine stretching vibrations occur at 228 and 287  $\text{cm}^{-1}$  and these probably represent the vibrations of the long and short bonds respectively<sup>19,20</sup>. The complex  $\text{Cu}(\text{quinoline})_2\text{Cl}_2$  on the other hand can not contain two bridging chlorine atoms of the above type, since the presence of the quinoline ring results in a copperchlorine long bond, a distance too great to give rise to a stretching frequency<sup>19</sup>. Thus the assignment of a copper chlorine stretching mode at 330  $\text{cm}^{-1}$  should represent the vibration of the copper chlorine short bond, which is also bridging in character. The far infra red spectra of a number of substituted quinoxaline derivatives of copper (II)

similarly indicate that for these compounds, terminal metal-chlorine bonds show absorption at 368-337  $\text{cm}^{-1}$  and bridging bonds occur at ca 320  $\text{cm}^{-1}$ <sup>21</sup>

Considering the available data it becomes evident that the values of copper halogen stretching frequencies are very much dependent upon the ligand used, even where the structures of the complexes are thought to be the same. From a study of copper-halogen frequencies Adams & Lock<sup>22</sup> have concluded that whereas the copper-chlorine stretching frequencies occur in the range 222-268  $\text{cm}^{-1}$ , those due to the copperbromine are observed from below 200 to 278  $\text{cm}^{-1}$ . The far infra red spectra of *o*-phenylenediamine copper (II) dichloride and dibromide show maxima at 316, 214  $\text{cm}^{-1}$  and 272,

190  $\text{cm}^{-1}$  respectively. It is reasonable to assign these to terminal ( $\text{Cl}^- = 316 \text{ cm}^{-1}$ ,  $\text{Br}^- = 272 \text{ cm}^{-1}$ ) and bridging ( $\text{Cl}^- = 214 \text{ cm}^{-1}$ ,  $\text{Br}^- = 190 \text{ cm}^{-1}$ ) copper-halogen units respectively by analogy with other complexes of copper (II) halides<sup>19</sup>. Similarly strong absorption bands observed in the region 300-252  $\text{cm}^{-1}$  and 260-116  $\text{cm}^{-1}$  for the chlorine and bromine complexes of the bis-diaminonaphthalene copper (II) and bis-diaminobiphenyl copper (II) are assigned to the (Cu-X) vibrations associated with non-bridging (axial) Cu-X units. These frequencies are in fair agreement with similar frequencies in complexes of the type  $\text{CuL}_2\text{X}_2$  in which the metal is known to be in a tetragonally distorted octahedral environment.<sup>23</sup>

The room temperature magnetic moments of the complexes are reported in Table I. The magnetic moment of copper (II) ion with an orbital doublet from the  $^2\text{D}$  state is given by:

$$\mu_{\text{eff}} = [S(S+1)]^{1/2} \left( \frac{1-2\lambda}{\Delta} \right)$$

where  $\lambda$  = spin orbit coupling constant and  $\Delta = 10D_q$ . The stereochemistry whether octahedral or tetragonal, however has little effect on the magnetic moment of the copper (II) ion<sup>24</sup>, having a spin orbit coupling constant  $\lambda = 850 \text{ cm}^{-1}$  and  $\mu_{\text{eff}} = 1.9-2.1 \text{ B.M.}$  The magnetic moments of the copper (II) diamine complexes were found to be within the range 1.84-2.02 B.M., normally observed for copper (II) complexes having an orbitally non degenerate ground state and an octahedral or distorted octahedral (tetragonal) environment about the copper (II) ion.

The solid reflectance spectra of the complexes are summarized in Table III. The complexes in general show broad bands in the region 14000-19000  $\text{cm}^{-1}$  with some evidence of a shoulder on the low frequency side. The reflectance spectra of  $\text{Cu}(\text{apda})\text{Cl}_2$  and the corresponding bromide have an irregular absorption band at the beginning of the visible region with a maximum at 14500  $\text{cm}^{-1}$ . The more intense absorption at ca 21000  $\text{cm}^{-1}$  is assumed to be a charge transfer band probably from filled halide p-orbitals to the hole in copper (II) d-shell, similar to that observed in the complexes of copper (II) having a square planar halide environment. The bis diamine complexes on the other hand show a broad band at about 15000  $\text{cm}^{-1}$  relatively insensitive to

Table 3. Reflectance Spectra between 7000 and 25000  $\text{cm}^{-1}$ .

Compound	$\nu_1 \text{ cm}^{-1}$	$\nu_2 \text{ cm}^{-1}$	$\nu_3 \text{ cm}^{-1}$
Cu(opda)Cl <sub>2</sub>	—	14000	21000
Cu(opda)Br <sub>2</sub>	—	14500	213000
Cu(opda) <sub>2</sub> Cl <sub>2</sub>	12000	14300	—
Cu(opda) <sub>2</sub> Br <sub>2</sub>	12500	14500	—
Cu(opda) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	—	18000	—
Cu(opda) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	14100	19100	—
Cu(opda) <sub>2</sub> SO <sub>4</sub> ·2H <sub>2</sub> O	14800	17500	—
Cu(dan) <sub>2</sub> Cl <sub>2</sub>	12100	15500	—
Cu(dan) <sub>2</sub> Br <sub>2</sub>	—	16000	—
Cu(dan) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	12500	18200	—
Cu(dan) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	14000	17700	—
Cu(dan) <sub>2</sub> SO <sub>4</sub> ·H <sub>2</sub> O	13800	17000	—
Cu(dabp) <sub>2</sub> Cl <sub>2</sub>	13200	15700	—
Cu(dabp) <sub>2</sub> Br <sub>2</sub>	—	16100	21000 <sup>br</sup>
Cu(dabp) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	—	17400*	—
Cu(dabp) <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	13600	17300	—
Cu(dabp) <sub>2</sub> SO <sub>4</sub> ·2H <sub>2</sub> O	12400 <sup>sh</sup>	15400	—

\*= Spectrum not well resolved, br=Broad sh=Shoulder.

changes in the axial positions. In the solid Cl<sup>-</sup>, Br<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>, this band is sharp and detached from the d-d transitions. In the solid SO<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> it appears as a well defined shoulder. The overall envelope shape (Fig. 2) in these latter cases is that usually found in tetragonally distorted copper (II) compounds<sup>25</sup>. In all cases the major d-d transitions occur between 15900 and 19000  $\text{cm}^{-1}$ , although in the halide complexes it appears to overlap the lowest charge transfer band, resulting in a very broad band (Fig. 2) depicting a D<sub>4h</sub> symmetry approximately.

The energy level diagram for ligand field of D<sub>4h</sub> symmetry would predict three transitions, while that for D<sub>2h</sub> would require four (Fig. 1). But as the [Cu(diamine)<sub>2</sub>]<sup>2+</sup> cations have approximate D<sub>4h</sub> symmetry, the splitting of the <sup>2</sup>E<sub>g</sub> level in this symmetry in going to D<sub>2h</sub> is not expected to be large. The precise order of the energy levels however is not certain. If we consider the diamines used to be sigma bounded ligands, the splitting of the <sup>2</sup>E<sub>g</sub> (O<sub>h</sub>) level will be greater than that of the <sup>2</sup>T<sub>2g</sub> (O<sub>h</sub>) level and the <sup>2</sup>B<sub>2g</sub> level will always lie below the <sup>2</sup>E<sub>g</sub> (D<sub>4h</sub>) level. Depending upon the degree of tetragonal distortion present three possible energy level sequences may arise:

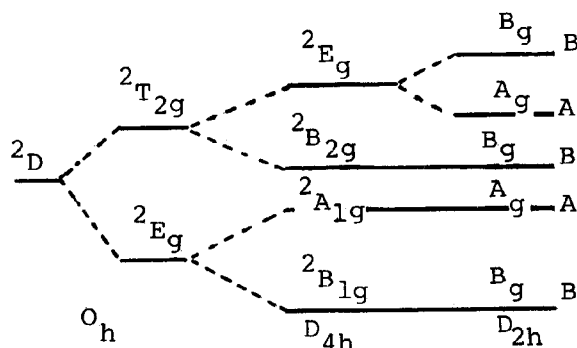


Fig. 1. Energy level diagram for a copper (II) ion in crystal fields of O<sub>h</sub>, D<sub>4h</sub> and D<sub>2h</sub> symmetry.

- (a)  ${}^2B_{1g} < {}^2A_{1g} < {}^2B_{2g} < {}^2E_g$ .
- (b)  ${}^2B_{1g} < {}^2B_{2g} < {}^2A_{1g} < {}^2E_g$ .
- (c)  ${}^2B_{1g} < {}^2B_{2g} < {}^2E_g < {}^2A_{1g}$ .

Case (a) will correspond to a low tetragonal distortion and (c) to a large tetragonal distortion, which might be found in true square coplanar complexes. Evidence for a true square coplanar Cu(II) cation is not

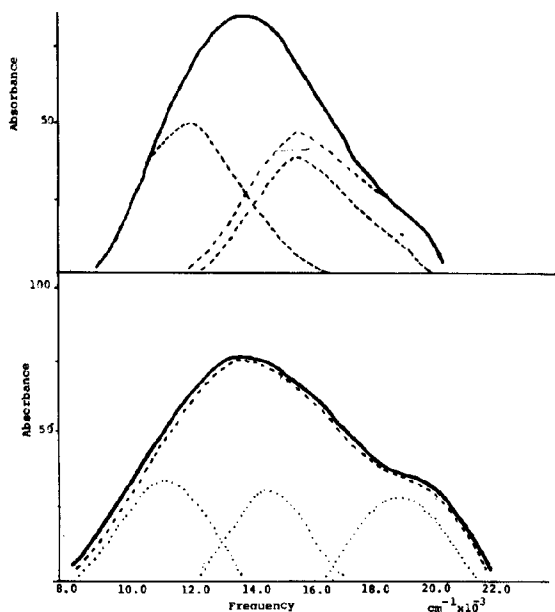


Fig. 2. Electronic Spectra (reflectance):

- a.  $\text{Cu}(\text{dabp})_2\text{Cl}_2$   
 b.  $[\text{Cu}(\text{dabp})_2](\text{ClO}_4)_2$

available, and all the Cu(II) complexes reported in the literature involve a tetragonal octahedral stereochemistry. As the transition  ${}^2B_{1g} \rightarrow {}^2E_g$  is likely to be the most intense transition<sup>27</sup>, the failure to locate a shoulder on the higher frequency side of the band maximum suggests that the sequence (c) above is unlikely in these complexes. The significant variation in the position of the lowest frequency band ( $\nu_1$ ) compared with the position of the two high frequency bands ( $\nu_2, \nu_3$ ) in all the complexes reported here suggest that it is reflecting the different degrees of tetragonal distortions present in these complexes, and support its assignment as the  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  transition. As the separation of the  ${}^2B_{1g}$  and  ${}^2A_{1g}$  levels with increasing tetragonal distortion will always be greater than that of the  ${}^2B_{2g}$  and  ${}^2E_g$  levels, the observation that the two high frequency bands, in general increase in frequency with increase in frequency of the  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  level, would also support this assignment. This would suggest that the bands listed as  $\nu_1, \nu_2$ , and  $\nu_3$ , in Table II should be tentatively assigned at the  ${}^2B_{1g} \rightarrow {}^2E_g$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$ , and  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  transitions respectively in a tetragonal symmetry  $D_{4h}$ .

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