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A series of phenoxo complexes of copper(II) containing a variety of halophenoxo ligands and a variety of amine ligands has been prepared. The thermal stability of the complexes with regard to the decom-

$$L_2Cu \left( O \left( O \right) \right)_2 \rightarrow L_2CuX_2 + \frac{2}{n} \left( O \left( O \right) \right)_n$$

was found to be lower with those ligands, L, which increase the oxidizing power of the copper(II) and vice versa.

The intense absorption bands in the visible region exhibited by these complexes have been assigned to a metal-to-ligand charge transfer process.

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position reaction:

#### Introduction

The preparation and properties of transition metal alkoxo derivatives have been studied in great detail (1). The aryloxo derivatives, on the other hand, have been virtually ignored, except for chelating ligands which utilize an aryloxy function. Although innumerable compounds are known containing such chelating ligands as salicylaldehydate, 8-hydroxyquinolinate, and 2-azophenolate, the specific properties of the aryloxy-metal bond have not been investigated.

A series of simple phenoxotitanium complexes was prepared by Funk *et al.* (2), from a variety of substituted phenols. More recently, a structural study by Watenpaugh and Caughlin (3) has shown the dimeric dichlorodiphenoxotitanium-(IV) to contain both linear and bridging phenoxo groups, as well as titanium in an unusual fivecoordinate state. The latter authors commented on the unusual color of phenoxotitanium complexes, but did not advance a satisfactory explanation.

The classical use of iron(III) for the colori-

metric determination of phenols has prompted several investigations (4, 5) to seek the origin of the characteristic intense colors obtained. There is general agreement that phenoxoiron(III) complexes are responsible for the colors, but the evidence is largely circumstantial and no stoichiometric complex has ever been isolated, or characterized.

A series of bis(phenoxo)bis(pyridine)copper-(II) complexes was prepared and characterized by Blanchard *et al.* (6) using a variety of substituted phenols. Such complexes are of considerable chemical interest because of the important industrial (7) and biological (8) role of copper(II) in the selective catalytic oxidation of phenols. A remarkable property of certain 4-halophenoxocopper(II) complexes is their tendency to undergo thermal decomposition (6), according to the generalized reaction [1], where L represents a neutral ligand and X is a halogen atom. It has been suggested (6) that the initiating step, both in reaction [1] and in the catalytic oxidative coupling of phenols (7), is ligand-to-

$$[1] \qquad nL_2Cu^{II} \underbrace{(0, -X)}_2 \rightarrow nL_2Cu^{II}X_2 + \underbrace{(0, -X)}_2$$

metal charge transfer to produce a phenoxy radical and a copper(I) species.

The present study was undertaken to answer two questions. Firstly, what is the dependence of the thermal stability of phenoxocopper(II) complexes on the nature of the neutral ligand. Secondly, what is the cause of the intense colors

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# TABLE I Analytical data for some phenoxocopper(II) complexes

		(	C	I	H	1	N	Chlo	oride
Phenol	Amine	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
2,4,6-Trichloro	Pyridine*	43.0	43.2	2.28	2.30	4.6	4.5	34.7	34.8
	$NH_3^{\dagger}$	29.3	28.8	2.04	2.2	5.7	5.8	43.4	43.8
	$C_2H_5NH_2^{\dagger}$	35.1	35.2	3.29	3.25	5.1	5.1	38.9	39.4
,,	Tetramethylen*	37.7	37.6	3.50	3.43	4.9	5.0	37.2	38.2
,,	Tetraethvlen*	42.0	41.8	4.45	4.45	4.5	4.4	33.9	34.5
,,	2.2'-Dipyridyl†	43.1	42.1	1.96	2.00	4.6	4.7	34.8	35.0
,,	o-Phenanthroline <sup>†</sup>	45.2	45.2	1.88	2.03	4.4	4.4	33.4	33.6
Pentachloro	Tetramethylen*	30.4	30.5	2.25	2.28	4.0	3.8	49.9	50.4
2,4-Dichloro	* ,,	42.9	42.6	4.37	4.42	5.6	5.5	28.2	28.6

\*Prepared by aqueous solution method. †Prepared by exchange with pyridine complex.

of phenoxocopper(II) complexes. (They are brown to purple in solution, dark brown to black crystals.)

#### Experimental

#### (1) Preparation of Phenoxo Complexes from Aqueous Solutions

Complexes derived from acidic phenols (in the present work this means those with at least two halide substituents) were prepared easily and in high yield from aqueous solutions of reagents. The standard procedure was to add the required amount of neutral ligand to a solution of CuSO<sub>4</sub>.5H<sub>2</sub>O (0.02 mole) in distilled water (50 ml). A second solution containing the phenol (0.04 mole) and sodium hydroxide (0.04 mole) in water (50 ml) was then slowly added to the copper solution with vigorous stirring. The resulting dark brown slurry was filtered, washed with water, and dried. Recrystallization of pyridine complexes was effected by dissolution in a minimum of hot benzene, filtration, and addition of excess methanol to the hot benzene filtrate. The tetramethyl- and tetraethylethylenediamine complexes were recrystallized from hot toluene-hexane solutions. The yields of these complexes were essentially quantitative. Analyses of some representative complexes are given in Table I.

#### (2) Preparation of Complexes from Bis(2,4,6-trichlorophenoxo)bis(pyridine)copper(II)

The high solubility of the pyridine complex in benzene permitted the simple preparation of other complexes by displacement of the pyridine in benzene solution.

Treatment of a hot saturated solution of the pyridine complex in benzene (about 5.0 g of complex in 50 ml of benzene) with a boiling solution of 2,2'-dipyridyl (1.6 g in 10 ml benzene), followed by dilution of the mixture with an equal volume of boiling hexane, yielded black crystals of the dipyridyl complex on cooling to room temperature. The yield (5.0 g) was essentially quantitative. The *o*-phenanthroline complex was prepared by the same method.

The ammonia, ethylamine, and ethylenediamine complexes were quite insoluble in benzene and could be precipitated by careful addition of the appropriate ligand to a benzene solution of the pyridine complex at room temperature. The ammonia complex was best prepared by bubbling gaseous ammonia into the benzene solution. The other amine ligands were added as solutions in benzene. Addition of excess of these saturated amine ligands resulted in the formation of ionic complexes by expulsion of the phenoxo ligand from the coordination sphere. The ionic complexes were blue, whereas the neutral complexes were light brown in the case of ammonia and ethylamine, and bright orange in the case of ethylenediamine.

Analyses of some derivatives prepared from the pyridine complex are given in Table I.

The orange bis(ethylenediamine) complexes with trihalophenols were also easily prepared by the aqueous solution method described above.

#### (3) Spectra of Complexes

Visible and ultraviolet spectra were measured with a Perkin–Elmer 202 recording spectrophotometer.

Infrared spectra were measured with a Perkin–Elmer Model 521 grating spectrometer. Samples were studied in carbon tetrachloride solution and dispersed in potassium bromide pellets.

# Results

## *Types of Phenoxocopper(II) Compounds*

Most amine ligands were found to yield tetracoordinate complexes of the type  $L_2Cu$ -(OPh)<sub>2</sub> (L = monofunctional amine ligand; OPh = halosubstituted phenoxo ligand) using the methods described above. A notable exception was ethylenediamine which yielded complexes containing two ethylenediamine ligands per copper(II) ion by both synthetic methods.

Saturated aliphatic amines (including ethylenediamine) in excess yielded blue ionic complexes, soluble in water, in which the phenoxo ligand had presumably been expelled from the coordination sphere. This phenomenon was not

#### HARROD: PHENOXO COMPLEXES OF Cu(II)



FIG. 1. Infrared spectra of (a) bis(trichlorophenoxo)diamminecopper(II), (b) copper(II)trichlorophenolate, and (c) sodium trichlorophenolate.

observed with unsaturated aromatic bases. In fact pyridine was found to be an excellent solvent for the  $Py_2Cu(OPh)_2$  complexes and their spectra were qualitatively the same in pyridine as in benzene. It may thus be concluded that pyridine has virtually no tendency to increase the

coordination number of these tetracoordinate complexes, nor to displace the phenoxo ligand.

A fourth type of complex was obtained by the aqueous solution method if the reaction was carried out in the absence of any added neutral ligand. The dark brown amorphous compounds

		Infra	red data	for trichlor	ophenox	ocopper(1	I) compl	exes*						
Neutral ligand						Absorpt	tion frequ	tency (cm	-1)					
C <sub>2</sub> Hs.NH2		1530		1450	-	1295	1240	1220				845	800) 785	740
NH₃		1530		1450		1298	1240	1230				858		740
None		1540		1435		126	5		1130		¢	848	$\begin{array}{c} 810 \\ 790 \end{array}$	750
2,2'-Dipyridyl		1530	-	460-1440		1312	1250					855	800	750
(CH <sub>3</sub> ) <sub>2</sub> N.CH <sub>2</sub> .CH <sub>2</sub> .N(CH <sub>3</sub> ) <sub>2</sub>		1525		1460		1310 1280	1245	1230				858		750
H <sub>2</sub> N.CH <sub>2</sub> CH <sub>2</sub> .NH <sub>2</sub>		1515		1465		1300	1240					840		730
Pyridine	1605	1527	1489	1455	1445	1305	1245	1210		1068	1040	855) 845)	800	760
(Py) <sub>2</sub> CuBr <sub>2</sub>	1605 1600		1490		1445			1220		1078	1040			753
Sodium trichlorophènolate		1525		1450		1310	1240	1220	1180			855	780	740
*Data altad for success in V D = nollate Can	and a state	form chow	in the point	ban official	intonoite of									

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Data cited for spectra in KBr pellets. Spectra in chloroform showed only minor shifts and intensity changes.

#### HARROD: PHENOXO COMPLEXES OF Cu(II)

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Thermal stability of trichlorophenoxocopper(II) complexes

Neutral ligand	Thermal behavior				
Biquinolyl, triphenylphosphine	Complexes too unstable to be isolated				
2,6-Dimethylpyridine	Stable enough to be isolated as solid. Lifetime in benzene $\sim$ hours at room temperature*				
Ammonia ethylamine	Rapid decomp. at $\sim$ 90 °C in solid state. Lifetime in benzene $\sim$ days at room temperature*				
Pyridine	Sharp decomp. at 125-127 °C in solid. Lifetime in benzene $\sim$ months at room temperature, * $\sim$ 12 h at 80 °C				
None	Sharp decomp. at 143–145 °C in solid				
2.2'-Dipyridyl	m.p., 175–177 °C; decomp. $\sim$ 195 °C				
Tetraethylethylenediamine	m.p., 167–168 °C				
Tetramethylethylenediamine <i>a</i> -Phenanthroline	m.p., 182–184 °C. Lifetime in benzene $\sim$ years† m.p., 220 °C: decomp. $\sim$ 220 °C				

\*These observations were made on numerous solutions prepared for spectroscopic and other measurements. †One solution of this complex which had been stored for two years, was found to be completely decomposed. The isolated polymer was found to have  $M_n \sim 80\ 000$ , by far the highest molecular weight ever obtained by thermal decomposition of phenoxy complexes.

obtained had the stoichiometry Cu(OPh)<sub>2</sub>, and were characterized by their almost complete insolubility. The only solvent found for these compounds was dimethylformamide and reprecipitation by addition of water to dimethylformamide solutions gave dark brown crystalline compounds containing coordinated dimethylformamide.

# Infrared Spectra of the Tetracoordinate

Complexes

Table II lists some of the principal infrared absorptions exhibited by a series of trichlorophenoxocopper(II) complexes. A comparison between the spectrum of the pyridine complex and the spectra of sodium trichlorophenolate and dibromobis(pyridine)copper(II), indicates that all of the bands of the former may be accounted for in terms of complexed pyridine and a trichlorophenolate anion, except for minor frequency shifts. The same is true of the other complexes, including the bis(ethylenediamine) complex. The only obvious deviation occurs with the simple copper trichlorophenolate which contains no neutral ligands.

The spectra of sodium trichlorophenolate, copper trichlorophenolate, and bis(trichlorophenoxo)diamminecopper(II) are shown in Fig. 1. The most significant variations in these spectra occur in the 1200–1300  $\text{cm}^{-1}$  region, the region in which the C-O vibrations of the phenoxy group are expected to occur. Although the ammine complex spectrum is somewhat different from that of sodium trichlorophenolate in this region, the difference is small compared to that of the copper trichlorophenolate.

# Thermal Stability of (Trichlorophenoxo)copper(II) Complexes

All of the trichlorophenoxo complexes thus far prepared were found to decompose according to eq. [1]. The ease of decomposition was found qualitatively to vary to a considerable degree, depending on the nature of the neutral ligand. Addition of biquinolyl, or triphenyl phosphine to benzene solutions of the pyridine complex resulted in rapid production of poly(dichlorophenyleneoxide) at room temperature, whilst the dipyridyl complex was stable for several years in benzene solution. Some qualitative data on the thermal decomposition of solutions, or pure compounds are shown in Table III.

In all cases of decomposition, the poly(dichlorophenyleneoxide) was isolated and characterized according to previously described procedures (6). The copper chloride complexes resulting from decomposition were only characterized in the case of the pyridine complex  $(Py_2CuCl_2)$ , the uncomplexed copper trichlorophenolate  $(CuCl_2)$ , and the tetramethylethylenediamine complex referred to in footnote (marked †) to Table III (dichlorotetramethylethylenediaminecopper(II)).

# Electronic Spectra of Phenoxocopper(II)

Complexes

The spectrum of bis(trichlorophenoxo)bis-(pyridine)copper(II) is shown in Fig. 2. This spectrum was typical of all the phenoxo complexes examined and may be discussed in terms of four regions.

A ligand band system in the 40 to 50 kK  $(1 \text{ kK} = 1000 \text{ cm}^{-1})$  region was observed in





methanol solution. Within the sensitivity and resolution of the instrument, these high energy ligand bands were not significantly altered by complexing and were not studied in any detail.

In benzene all of the complexes examined obeyed the Beer-Lambert law. Three band systems were observed at  $\lambda_{max} \sim 35$ ,  $\sim 27$ , and  $\sim 20$  kK. The spectrum of the tetramethylethylenediamine complex is shown in Fig. 3. The 35 kK band system, arising, at least partly, from a phenolate ligand transition, was strongly perturbed by varying the neutral ligands of the complex. The changes occurring in this band, with trichlorophenoxocopper(II) complexes, are illustrated for several neutral ligands in Fig. 4. The 27 kK band appeared as a shoulder on the low energy tail of the 35 kK band, and was present in all of the complexes examined. This band did not appear to change intensity, or position, on varying the neutral ligands.



FIG. 3. Spectrum of bis(trichlorophenoxo)-N,N,N',-N'-tetramethylethylenediaminecopper(II) in the ultraviolet–visible region (in benzene solution).

The band in the 19 to 23 kK region is mainly responsible for the intense colors of the phenoxocopper(II) complexes. The absorption maximum for this band was found to undergo shifts on substituting different neutral ligands into a given phenoxo complex. Data for a number of complexes in benzene and other solvents are given in Table IV.



FIG. 4. Effect of amine ligands on the 35 kK band system of trichlorophenoxocopper(II) complexes. \_\_\_\_\_, pyridine; \_\_\_\_\_, NH<sub>3</sub>; \_\_ $\Delta$ \_\_, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>; \_\_O\_\_, tetramethylethylenediamine; \_\_\_\_\_, tetratethylethylenediamine.

# The Structure of Phenoxocopper(II) Complexes

Chemical analysis, molecular weight data, and infrared spectra obtained in the present study and those reported in ref. 6, all indicate that the majority of phenoxocopper(II) complexes are four-coordinated and monomeric.

A determination of the crystal structure of bis(trichlorophenoxo)N,N,N',N' tetramethylethylenediaminecopper(II) has recently been completed (9). In this complex the copper(II) ion is coordinated by two nitrogens and two oxygens in an approximately square planar arrangement. There is a small tetrahedral distortion giving an angle of ca. 20° between the N—Cu—N and the O—Cu—O planes. A schematic representation of the molecule is shown in Fig. 5.

Perhaps the most important property of this molecule, as far as the present study is concerned,

Neutral ligand	Solvent	Phenol	v <sub>max</sub> (kK) (±0.02)	$\epsilon_{max} \times 10^{-3}$
$(C_2H_5)_2N.CH_2.CH_2.N(C_2H_5)_2$	Benzene	2,4,6-Trichloro	19.76	3.3
o-Phenanthroline	**	**	20.14	3.1
2.2'-Dipyridyl			20.35	2.0
(CH <sub>4</sub> ) <sub>2</sub> N CH <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub>		••	20.54	2.5
Pyridine			22.51	1.1
NHa	,,	,,	22.55	1.3
C.H. NH.	**	**	22 65	13
26 Lutidine*	**	**	24 18	1.5
(CU) N CU CU N(CU)	,,	"," Pentachloro	24.10	
$(C\Pi_3)_2$ . N. $C\Pi_2$ . $C\Pi_2$ . N $(C\Pi_3)_2$	>>	2 4 Dishlara	20.40	
»»	,,	2,4-Dicilioro	20.63	
»*		4-Chioro	22.00	
Pyridine	Pyridine	2,4,6-Trichloro	21.9	1.0
**	Hexane	37	22.7	1.0
**	Tetrahydrofuran	**	22.9	1.0
	Chloroform		22.7	1.2
	Ethanol		$\sim 25.0$	0.7
27	Methanol	"	~25.0	0.5
,,		,,	20.0	5.5

	TA	ABLE IV	
Spectroscopic	data for	phenoxocopper(II)	complexes

\*Due to their instability, these solutions were of doubtful purity.



FIG. 5. Structure of bis(trichlorophenoxo)tetramethylethylenediaminecopper(II). (After Vogt, La Placa, and Bednowitz, see ref. 9.)

is the Cu—O—C bond angle of ca. 120° and the resulting very close approach of the two rings of the phenoxo ligands. That this close approach was not primarily responsible for the charge transfer bands observed in the present study may be concluded from the fact that these bands were also observed in the complexes with monodentate ligands. The pyridine complex had no detectable dipole moment and must be *trans*, a configuration which would make close approach of the ligand rings impossible.

#### Discussion

Thermal Stability of Trichlorophenoxo Complexes If, as has been previously suggested (6), the initiation step in the thermal decomposition reaction [1] is a ligand-to-metal electron transfer,

the nature of the neutral ligand should strongly influence the thermal stability of the starting complex. After a thorough study of the effect of amine ligands on the redox potential of the Cu(II)/Cu(I) system, James and Williams (10) concluded that the order for stabilization of Cu(II) was ethylenediamine  $\gg 2,2'$ -bipyridyl >1,10-phenanthroline > pyridine  $\sim$  ammonia  $\gg$  2,2'-biquinolyl. The most important factors governing this sequence were the chelate effect (Cu(II) forms chelates readily, Cu(I) is reluctant to form chelates) and the  $\pi$ -acceptor property of the ligand. The latter was invoked by James and Williams (10) to explain the order of potentials of the dipyridyl and phenanthroline complexes. The anomalous position of the biquinolyl ligand in the series was attributed to its poor ability to chelate, due to steric interference by the 8,8' hydrogens.

In the present study a striking correlation was found to exist between the thermal stability of phenoxocopper(II) complexes and the position of the amine ligand in the James and Williams sequence of oxidation potentials. Those complexes containing amine ligands which preferentially stabilize copper(I) were found to be markedly less stable than those containing ligands expected to enhance the stability of copper(II). Although no oxidation potential data are available for tetraalkylethylenediamine complexes, they would certainly be expected to stabilize copper(II) and the phenoxo complexes containing such ligands were found to be exceptionally resistant to thermal decomposition.

# The Electronic Spectra of Phenoxocopper(II) Complexes

The outstanding feature of the visible– ultraviolet spectra of phenoxocopper(II) complexes is the general occurrence of an intense band in the 20 kK region. The intensity of this band is too high for a simple  $d \rightarrow d$  transition and at first sight it was tempting to assign the band to a ligand-to-metal charge transfer process. Examination of the experimental observations argued against such an assignment. The evidence may be summarized as follows:

(*i*) Complexes with a low energy ligand-tometal charge transfer would be expected to decompose more readily than those with a higher energy charge transfer. In fact, complexes which have absorption at lower energy have been found to be much more thermally stable than complexes with absorption at high energy.

(*ii*) The thermal stability of complexes follows the sequence of oxidation potentials for Cu(I)/ Cu(II) couples in the presence of various amine ligands. For example, the thermal stability of 2,4,6-trichlorophenoxo complexes was found to be in the sequence: *o*-phenanthroline  $\sim$  bipyridyl > pyridine  $\sim$  NH<sub>3</sub> > biquinolyl. The energy of the 20 kK band followed the inverse of this sequence.

(*iii*) In the series of complexes of 4-chloro-, 2,4-dichloro-, 2,4,6-trichloro-, and pentachlorophenol, with the same neutral ligand, the absorption moves progressively to lower energy. This shift is in a direction contrary to that expected for a ligand-to-metal charge transfer, on the basis of the expected ease of oxidation of the corresponding phenoxide ion.

This evidence strongly suggests the origin of the 20 kK band to be a metal-to-ligand charge transfer, rather than the reverse. On the basis of chemical intuition, the latter proposition seems unlikely. In effect, it requires the donation of an electron by Cu(II), a good oxidizing agent, to a phenoxide ion, already carrying negative charge and normally considered to be a reducing species. However, a qualitative study of the ligand and metal energy levels indicates that such a transition is not unlikely.

The existence of metal-to-ligand charge transfer has been postulated and discussed at



FIG. 6. Schematic molecular orbital diagram for a *cis*-bis(phenoxo)copper(II) complex.

some length by Jørgensen (11). He suggested that charge transfer bands in certain pyridine and *o*-phenanthroline complexes may originate from the excitation of an electron in an atomic-like orbital on the metal ion to an antibonding  $\pi^*$ orbital on the ligand. Such a transition could certainly be postulated to occur in phenoxo complexes.

A qualitative molecular orbital energy level diagram for *cis*-bis(trichlorophenoxo) complexes is shown in Fig. 6. It is assumed that the molecule exhibits ideal  $C_{2v}$  symmetry and that the neutral ligands only contribute orbitals of  $\sigma$  symmetry. The phenoxo ligands were assumed to contribute  $\sigma$ -orbitals, a set of low energy and a set of high energy  $\pi$ -orbitals. The molecular orbital diagram for a *trans*-complex  $(D_{2h})$  would not differ qualitatively from Fig. 5, nor would the inclusion of  $\pi$ -orbitals from the neutral ligands cause serious change.

The existence of metal-to-ligand charge transfer may be understood in terms of excitation from  $b_2^{m}$ , or  $a_1^{m}$  orbitals (largely associated with the metal) to  $b_2^{*}$ , or  $a_2^{*}$  orbitals (ligand antibonding  $\pi$ -orbitals associated largely with oxygen). Similarly, a ligand-to-metal charge

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transfer band would be expected as a result of excitations from the highest energy  $a_1 \sigma$ -bonding orbital, and/or the  $a_2$  and  $b_2$   $\pi$ -bonding orbitals to  $a_1^{\text{m}}$ . Such transitions are almost certainly responsible for the manifold of bands in the 35 kK region (c.f. Fig. 3). It is interesting to note that the latter bands do in fact extend to lower energy in those complexes exhibiting poor thermal stability. The shifts of the 20 and 35 kK band systems in opposing directions suggest that the primary effect of the amine ligands is to raise, or lower, the metal orbitals relative to the phenoxo ligand orbitals.

The effect of solvent on the metal-to-ligand charge transfer is not easily interpreted. Solvation at the vacant coordination positions above and below the plane of the complex should raise the average energy of the metal orbitals. The low value for the transition energy in pyridine compared to hexane, benzene, and chloroform is in accord with such an interpretation. The slightly higher value in tetrahydrofuran and the much higher values in methanol or ethanol, must, however, be considered anomalous. In the latter solvents a specific effect, such as hydrogen bonding to the phenoxy oxygen, may be operative.

#### Conclusions

The properties of phenoxocopper(II) complexes indicates that phenolate ligands can participate in both metal-to-ligand and ligandto-metal charge transfer. In the case of copper(II) complexes, both types of transition are at relatively low energy and the energies of the transitions are quite sensitive to the character

of both the phenolate and the other ligands present in the complex.

At present the most probable initiation step for decomposition of phenoxocopper(II) complexes involves homolysis of the Cu-O bond via ligand-to-metal charge transfer. There is no evidence to date to suggest that the low energy metal-to-ligand charge transfer has any relationship to the chemistry of decomposition. A detail study of the kinetics and mechanism of this reaction is in progress.

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