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New complexes of copper cinnamates and imidazole or substituted imidazole

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Abstract

We have prepared five new organo-metallic complexes of imidazoles and a dicarboxylate, copper cinnamate, which may be considered as extremely simple models of the active centres in most biocatalysts. The thermal behaviour of the complexes was studied. Using ESR and diffuse reflectance spectra, monomeric or dimeric species were detected.

INTRODUCTION

Because many metalloenzymes and proteins have structures that have yet to be clearly determined, it seemed interesting to prepare some new organo-metallic complexes. Binding between metal(II) ions and imidazole ligands occurs frequently in nature, as many metalloproteins are coordinated by the imidazole side-chains of histidyl residues. These complexes may be considered as extremely simple models of the active centres in most biocatalysts. Metal coordination compounds containing imidazole ligands have been synthesized for many years and have been studied intensively, both structurally and spectroscopically [1–6].

Several mixed ligand complexes of copper(II) have previously been studied but it appears that complexes involving imidazoles and dicarboxylates have not yet been described. We report here the preparation and thermal analysis of such complexes where the dicarboxylate is cinnamate; their electron spin resonance (ESR) and diffuse reflectance spectra are also reported.

Five complexes involving Cu(II) cinnamate and imidazole or substituted imidazole were prepared.

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EXPERIMENTAL

Preparation

A mixture of $CuSO_4 \cdot 5H_2O$ and imidazole or substituted imidazole was heated with magnetic stirring in 100 cm^3 ethanol. The mixture was allowed to reflux for two hours and then the hot mixture was filtered. The blue solution obtained was left to crystallize (compounds **II** and **V**). For the other complexes (**I**, **III** and **IV**), a blue-green powder was obtained after filtration. The following compounds were obtained:

I $(C_6H_5–CH=CH–COO)_2Cu \cdot (\text{imidazole})_2 \cdot H_2O$
II $(C_6H_4–CH=CH–COO)_2Cu \cdot (\text{1-methyl imidazole})_4 \cdot H_2O$
III $(C_6H_5–CH=CH–COO)_2Cu \cdot (\text{2-methyl imidazole}) \cdot (H_2O)_2$
IV $(C_6H_5–CH=CH–COO)_2Cu \cdot (\text{4-methyl imidazole}) \cdot (H_2O)_2$
V $(C_6H_5–CH=CH–COO)_2Cu \cdot (\text{1,2-dimethyl imidazole})_2 \cdot (H_2O)_2$

Another method was necessary to obtain compound **0** $(C_6H_5–CH=CH=CH–COO)_2Cu$. A mixture of Cu powder and cinnamic acid in absolute alcohol was refluxed for seven days. A fine blue powder was obtained and dried in air.

Chemical analysis

The metal content was determined by EDTA titration. The cinnamate and imidazole or substituted imidazole contents in the complexes were determined by potentiometric titration with $HClO_4$ in acetic anhydride. The curves obtained showed two inflexion points, the first corresponding to the neutralization of imidazole, the second corresponding to the neutralization of the cinnamate ion. The water content in the samples was further confirmed by thermogravimetry. All results support the formulae given above.

Thermal studies

Additional studies were carried out by thermogravimetry to confirm the molecular formulae assumed on the basis of elemental analysis and to determine the water content in each complex. The measurements were performed in air over the temperature range 293–1293 K at a heating rate of 10 K min^{-1} using a TG and DTA coupled Setaram 85 microbalance. Thermoanalytical diagrams for the complexes are shown in Figs. 1 and 2.

For all hydrated compounds, the initial temperature of decomposition

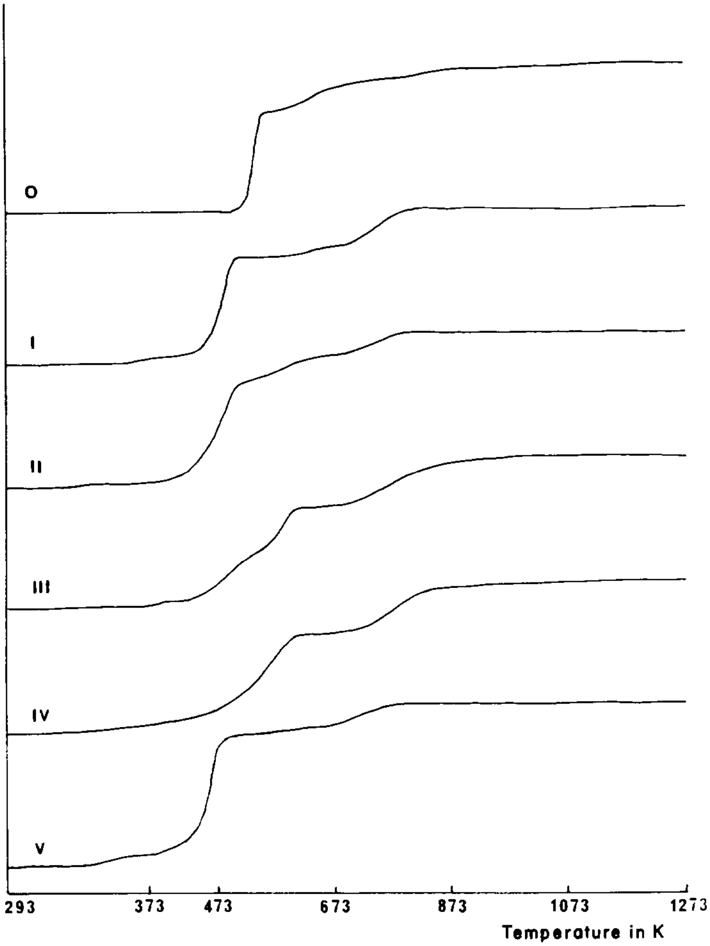

Fig. 1. TG curves in air.

was in the range of 350 K. They all lost water molecules in one step, except compound **III**. After the plateau corresponding to the anhydrous compound, a complex decomposition occurs, leading at about 600–650 K to a second plateau. We assume that this intermediary corresponds to compound X. The composition of compound X seems to be close to $Cu(COO)_2Imid$ or $Cu(COO)_2(MeImid)_x$ where $x = 1$ or 2. The analytical analysis of the mixture obtained and the percentage weight loss after this intermediary gave results agreeing with those expected. After this second plateau, the next weight loss suggests CuO and we note an intense exothermic peak on the DTA curve.

The general decomposition scheme is summarized below. The compounds in square brackets were assumed but not isolated. (W.L. = weight loss).

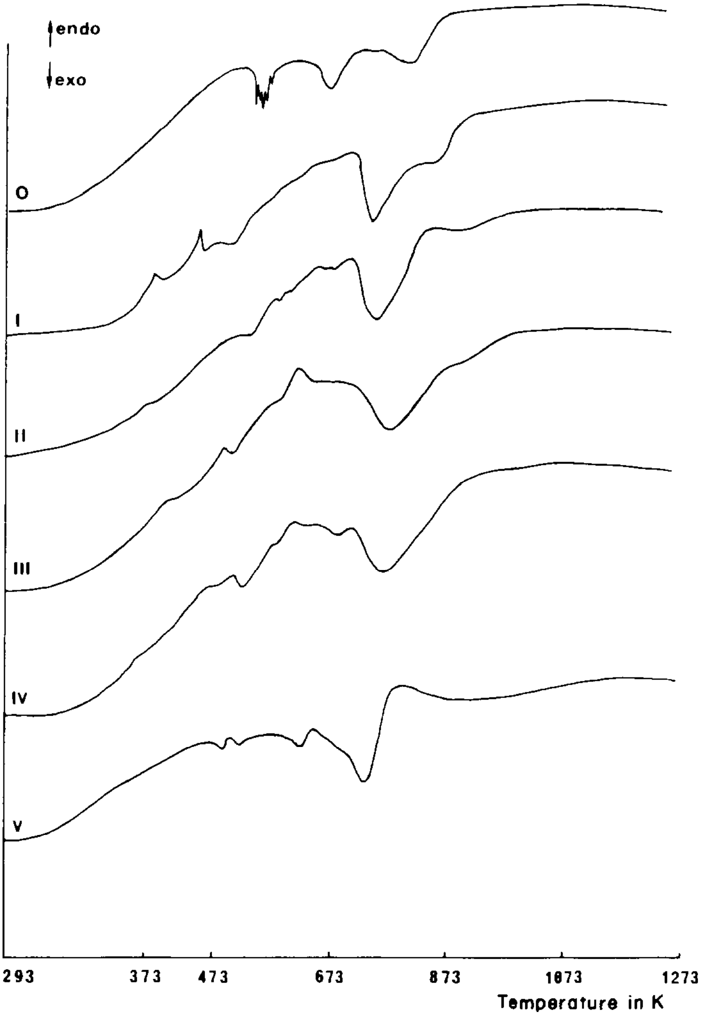

Fig. 2. Thermal differential curves in air.

Compound 0

$(C_6H_5\text{-}CH{=}CH\text{-}COO)_2Cu \xrightarrow[\text{DTA 483–562 K (endo)}]{\text{TG 483–562 K}}$

$[(CH_3COO)_2Cu] \xrightarrow[\text{DTA 562–607 K}]{\text{TG 562–607 K}} [(COO)_2Cu] \xrightarrow[\text{DTA 607–708 K (exo)}]{\text{TG 607–708 K}}$

W.L. th., 49.3% W.L. th., 57.6%

W.L. exp., 50.5% W.L. exp., 56.7%

$[CuCO_3] \xrightarrow[\text{DTA 708–1266 K (endo)}]{\text{TG 708–1266 K}} CuO$

W.L. th., 65.45% W.L. th., 77.77%

W.L. exp., 65.35% W.L. exp., 76.25%

Compound **I**

$$(C_6H_5\text{–}CH{=}CH\text{–}COO)_2Cu(Imid)_2 \cdot H_2O \xrightarrow[\text{DTA 388–395 K (endo)}]{\text{TG 388–395 K}}$$

$$[C_6H_5\text{–}CH{=}CH\text{–}COO)_2Cu(Imid)_2] \xrightarrow[\text{DTA 395–500 K}]{\text{TG 395–500 K}}$$
W.L. th., 3.5%
W.L. exp., 3.22%

$$[Cu(COO)_2Imid] \xrightarrow[\text{DTA 500–751 K (exo)}]{\text{TG 500–751 K}}$$
W.L. th., 57.08%
W.L. exp., 56.63%

$$[CuCO_3] \xrightarrow[\text{DTA 751–858 K}]{\text{TG 751–858 K}} CuO$$
W.L. th., 75.84% W.L. th., 84.46%
W.L. exp., 72.75% W.L. exp., 83.83%

Compound **II**

$$(C_6H_5\text{–}CH{=}CH\text{–}COO)_2Cu(Me_1Imid)_4 \cdot H_2O \xrightarrow[\text{DTA 310–330 K (endo)}]{\text{TG 310–330 K}}$$

$$[(C_6H_5\text{–}CH{=}CH\text{–}COO)_2Cu(Me_1Imid)_4] \xrightarrow[\text{DTA 330–600 K}]{\text{TG 330–600 K}}$$
W.L. th., 2.57%
W.L. exp., 2.56%

$$[Cu(COO)_2(Me_1Imid)_2] \xrightarrow[\text{DTA 600–754 K (exo)}]{\text{TG 600–754 K}}$$
W.L. th., 54.89%
W.L. exp., 55.10%

$$[CuCO_3] \xrightarrow[\text{DTA 754–1000 K (endo)}]{\text{TG 754–1000 K}} CuO$$
W.L. th., 82.33% W.L. th., 88.63%
W.L. exp., 80.92% W.L. exp., 87.86%

Compound **III**

$$(C_6H_5\text{–}CH{=}CH\text{–}COO)_2Cu(Me_2Imid)(H_2O)_2 \xrightarrow[\text{DTA 328-424 K (endo)}]{\text{TG 328–424 K}}$$

$$[(C_6H_5\text{–}CH{=}CH\text{–}COO)_2Cu(Me_2Imid)\cdot H_2O] \xrightarrow[\text{DTA 424–650 K (endo)}]{\text{TG 424–650 K}}$$

W.L. th., 3.78%
W.L. exp., 3.72%

$$[Cu(COO)_2Me_2Imid] \xrightarrow[\text{DTA 650–840 K (exo)}]{\text{TG 650–840 K}}$$

W.L. th., 50.88%
W.L. exp., 49.13%

$$[CuCO_3] \xrightarrow[\text{DTA 840–1191 K}]{\text{TG 840–1191 K}} CuO$$

W.L. th., 74.01%	W.L. th., 83.27%
W.L. exp., 74.44%	W.L. exp., 82.66%

Compound **IV**

$$(C_6H_5\text{–}CH{=}CH\text{–}COO)_2Cu(Me_4Imid)(H_2O)_2 \xrightarrow[\text{DTA 314–445 K (endo)}]{\text{TG 314–445 K}}$$

$$[(C_6H_5\text{–}CH{=}CH\text{–}COO)_2Cu(Me_4Imid)] \xrightarrow[\text{DTA 445–621 K (endo)}]{\text{TG 445–621 K}}$$

W.L. th., 7.56%
W.L. exp., 8.11%

$$[Cu(COO)_2Me_4Imid] \xrightarrow[\text{DTA 621–1000 K (exo)}]{\text{TG 621–1000 K}}$$

W.L. th., 56.92%
W.L. exp., 53.07%

$$[0.5\ CuCO_3 + 0.5\ CuO] \xrightarrow[\text{DTA 1000–1266 K (endo)}]{\text{DG 1000–1266 K}} CuO$$

W.L. th., 79.29%	W.L. th., 83.28%
W.L. exp., 80.71%	W.L. exp., 82.92%

Compound **V**

$$(C_6H_5\text{–}CH{=}CH\text{–}COO)_2Cu(diMe_{1\text{–}2}Imid)_2(H_2O)_2 \xrightarrow[\text{DTA 312–346 K (endo)}]{\text{TG 312–346 K}}$$

$$[(C_6H_5\text{–}CH{=}CH\text{–}COO)_2Cu(diMe_{1\text{–}2}Imid)_2] \xrightarrow[\text{DTA 346–535 K (endo)}]{\text{TG 346–535 K}}$$

W.L. th., 6.13%
W.L. exp., 6.11%

$$(Cu(COO)_2(diMe_{1\text{–}2}Imid)] \xrightarrow[\text{DTA 535–732 K (exo)}]{\text{TG 535–732 K}}$$

W.L. th., 57.72%
W.L. exp., 57.65%

$$[\mathrm{CuCO_3}] \xrightarrow[\text{DTA 732–1209 K (endo)}]{\text{TG 732–1209 K}} \mathrm{CuO}$$

W.L. th., 78.9% W.L. th., 87.79%
W.L. exp., 78.29% W.L. exp., 87.65%

Spectral studies

Electron paramagentic resonance

The X-band first-derivative ESR spectra were recorded for the powdered samples at room temperature and liquid nitrogen temperature at 77 K with a Brucker spectrometer equipped with a dual cavity, see Figs. 3 and 4.

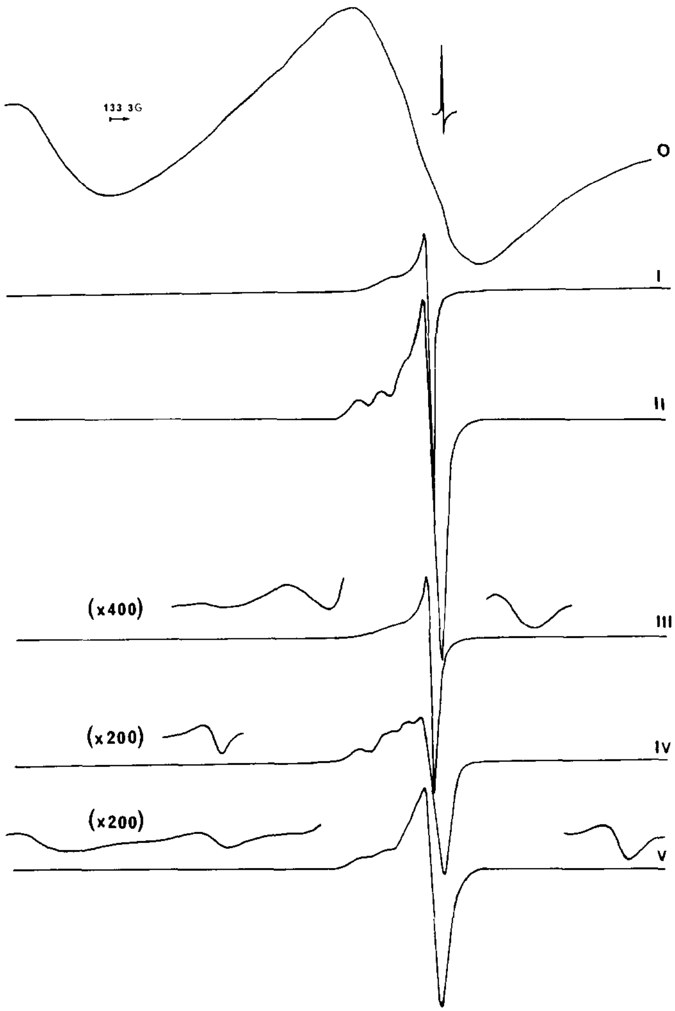

Fig. 3. ESR spectra at 293 K.

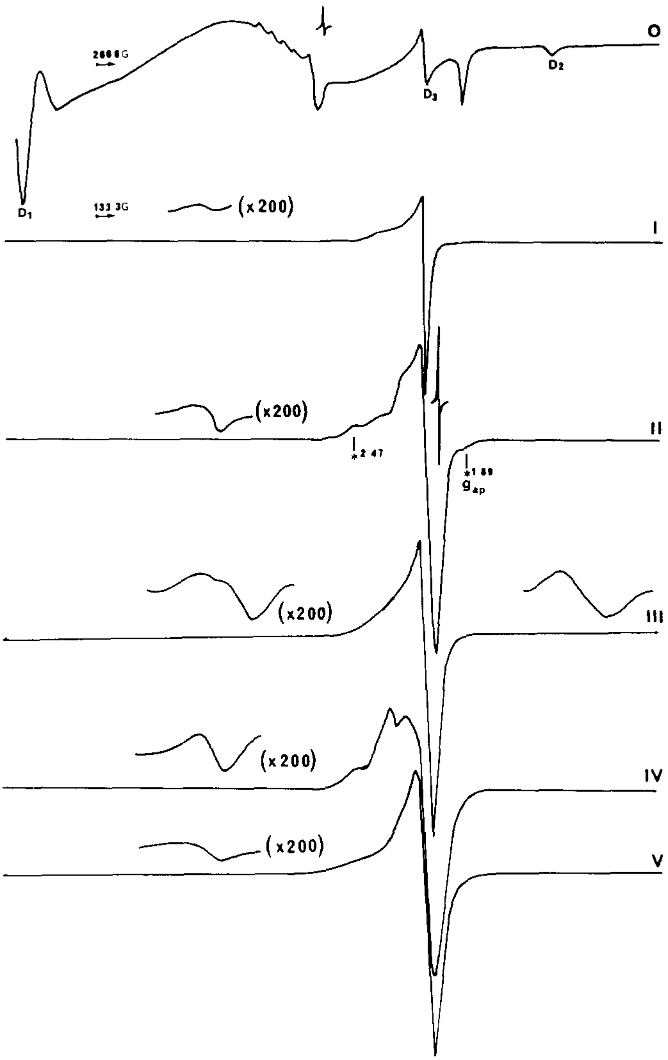

Fig. 4. ESR spectra at 77 K.

Strong pitch Varian was used as a reference for the g determination ($g_{sp} = 2.0028$).

Sample **0** exhibits an ill-defined spectrum at room temperature consisting of a wide line centred at $g = 2.2$, and a low-field component which suggests the presence of dimeric species with large D values. Such large D values are very often observed with copper carboxylates (copper chloropropionate, $D = 35.7\ \mathrm{m}^{-1}$ [7] and copper acetate monohydrate, $D = 30\ \mathrm{m}^{-1}$ [8]).

The recorded spectra are more complex at 77 K (Fig. 4). Narrow lines develop on a background consisting of a wide line centred near 2.2 (g value). Small amounts of monomeric species are clearly observed. The

TABLE 1

ESR parameters of initial compound **0**, copper cinnamate

Parameters	77 K
Monomer	
g_1	2.063
g_2	2.068
g_3	2.357
a_1/gauss	32
a_2/gauss	43
a_3/gauss	121
Dimer	
H_1/gauss	162
H_2/gauss	5861
H_3/gauss	4476
	4901
$g_\parallel$	2.372
$g_\perp$	2.067
D/m^{-1}	33.3
$E' = E(\mathrm{gauss})/g_0\beta$	1.07 m^{-1}

corresponding g and a values are given in Table 1. Lines D_1, D_2, D_3 are due to the presence of dimeric copper species. The splitting of the D_3 line for sample **0** shows that we have to consider an E term in the spin hamiltonian. The g values, and D and E terms can be calculated using the formula given by Sharrock et al. [9]. A further hypothesis is necessary to complete the calculations: the gx, gy anisotropy is sufficiently small to consider to a first approximation that $gx \approx gy = g$. The calculated values are given in Table 1. The complexes obtained after reaction with imidazole or methyl imidazole exhibit a more or less symmetrical line generally assigned to mononuclear species. In the case of such species ($S = 1/2$) with axial symmetry, the g values are taken, when possible, at the extrema of the derivative; the mean g values (g) were measured at the zero point of the derivative.

For all samples except **I**, the shape of the ESR signal is affected by the temperature (Fig. 4). Spectra were difficult to interpret because of the superimposition of lines coming from several species. The main constituent is a mononuclear copper complex for which it is difficult to give accurate g and a values (Table 2).

The disappearance of copper hyperfine structure in the parallel region at low temperature (compounds **IV** and **V**) could indicate small structural changes resulting in greater dipolar interactions. In the spectra of compounds **II**, **IV** and **V**, a low intensity band corresponding to the $\Delta m_s = 2$ transition indicates traces of dimer in the monomer. For

TABLE 2

ESR parameters of different complexes

Compound	$g_\perp$ 298 K	$g_\parallel$ 298 K	g 298 K	$a_\parallel$/gauss 298 K	D/m^{-1} 298 K	$g_\perp$ 77 K	$g_\parallel$ 77 K	g 77 K	$a_\parallel$ 77 K	D/m^{-1} 77 K	Purity at 298 K
I	2.06(6)	2.29	2.07(8)			2.06(6)	2.29	2.02(8)			Pure monomer
II monomer **II** dimer	2.00(5)	2.27 2.21	2.06	175	4.77	2.01(1)	2.26 2.22	2.06(6)	180	5.05	Monomer + dimer
III monomer **III** dimer	2.04(8)	2.26 2.15	2.06(7)		9.55		2.12			14.4	Monomer + dimer traces $r_{\mathrm{Cu-Cu}} = 3.15$ Å at 298 K
IV monomer **IV** dimer	2.00(5)	2.25 2.21	2.07(1)	180		2.02	(2.47 2.21	2.08(1)		3.25	Monomer + dimer traces with large D value
V monomer **V** dimer traces (int. comp.)	2.02(1)	2.27	2.06(7)	180		2.02(8)	(2.48 2.23	2.07(2)		3.17	Monomer + dimer traces of initial compound

compound **III**, the same interpretation that was applied to chloropropionate [7] using the model of Chikira and Kon [10], was used to give approximate values of D and $g_{\parallel}$. For this compound, the lowering of the temperature strongly affects the ESR spectrum and a change in colour has been observed on cooling. A second set of g and D values have been deduced (Table 2) from the ESR spectra, and structural changes with temperature have to be considered for this compound. Calculation of r_{Cu-Cu} values (Table 2) give significant values at room temperature. For sample **II**, the presence of a line at $g_{ap} = 1.89$ has been associated with that at 2.47 (indicated by a star in Fig. 4) leading to the D and g values in Table 2. This D value is slightly higher than those tabulated for samples **IV** and **V**. To obtain the D values, we considered that the line around 2.48 has to be associated with another line which cannot be detected because it is obscured by the perpendicular part of the spectrum coming from mononuclear species ($g_{\perp} \approx 2.07$). According to these considerations, we have reexamined copper chloropropionates complexes with imidazoles.

Diffuse reflectance spectra

Diffuse reflectance spectra were recorded at room temperature (Fig. 5) for all the compounds on a Beckmann UV 5240 spectrophotometer, over the range 40 000–4000 cm^{-1} (Fig. 5). A Kodak white reflectance standard was used as a reference and for dilution of the copper samples (10 wt.%).

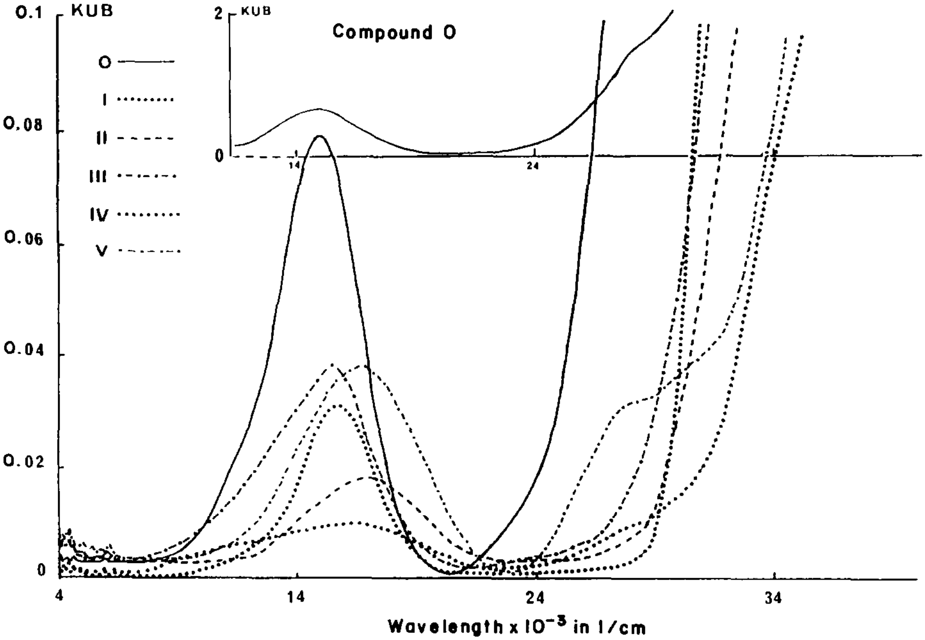

Fig. 5. Reflectance spectra.

TABLE 3

Reflectance parameters

Compound	$\Delta E_{max}/cm^{-1}$
Compound **0**	10900 (shoulder), 15100, 27650, 40000
Compound **I**	15750
Compound **II**	17050
Compound **III**	16672, 28240
Compound **IV**	18250, 27950
Compound **V**	15650, 26240 (shoulder)

In the near IR, sharp peaks of weak intensity correspond to harmonics and combination bands of fundamental vibrations in the ligands. These bands are very difficult to assign. For the compound **0** (Table 3) in which a copper pair was evidenced by ESR, we observed three absorption bands at 15 100 (with a shoulder at 10 900), 27 650 and 40 000 cm^{-1}. The first band arises from a ligand field transition. The last is assigned to a charge transfer absorption [11]. Attribution of the band at around 28 000 cm^{-1} differs in the literature [7]. This band is missing in the imidazole and cinnamate complexes that are considered as mainly mononuclear from ESR analysis. It is clearly present in **III** and **IV** for which traces of binuclear species have been detected.

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