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STUDY OF COPPER(II) CHLOROPROPIONATES COMPLEXED WITH IMIDAZOLE OR METHYL SUBSTITUTED IMIDAZOLES

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ABSTRACT

The preparation of complexes involving copper(II) chloropropionates and imidazole or methyl substituted imidazoles is described. The results of thermal and spectral studies are reported for the different complexes. The monomeric character of these complexes is shown; in addition, the dimeric character of the initial compound is noted. *D* and *E* values are given for the dimer compounds.

INTRODUCTION

Organic complexes of paramagnetic ions, and particularly those of copper(II), possess interesting catalytic properties, resulting in their catalytic action in living organisms. These complexes may be considered as extremely simple models of the active centres in most biocatalysts. The presence of donor ligands in addition to the carboxylates has also been shown to have a marked effect on whether or not a dinuclear complex is formed. For example, copper(II) formate and the formate tetrahydrate form polymeric structures, whereas the monopyridine adduct is dimeric [1].

Imidazole is an excellent donor towards metal ions, showing a great diversity in the types of complex formed. A limited amount of work has been published [2] on imidazole and related ligands, and a more exhaustive

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study of the complexing properties of such compounds, both in solution and in the solid state, has been undertaken [3–9]. In view of the potential use of 1,2-dimethylimidazole as a herbicide, and since its coordination behaviour could not readily be predicted from previous work, it was of interest to examine the complexes it forms with a variety of halogen substituted alkanoates.

In this work, the preparation and spectral and magnetic properties of some of the imidazole complexes are reported, in order to obtain further information on the effects of these additional ligands on the exchange interaction.

EXPERIMENTAL

Preparation

Two different experimental approaches have been used, each leading to the same final products. In the first, a mixture of 2- or 3-chloropropionic acid, $CuCO_3$, $Cu(OH)_2$, $n H_2O$ and imidazole or substituted imidazole in absolute alcohol was allowed to reflux for 2 h. The hot mixture was filtered and evaporated until blue crystals separated. These crystals were washed with alcohol and dried in air. In the second method, the alcoholic mixture heated under reflux for 2 h consisted of $(CH_2ClCH_2COO)_2Cu$ or $(CH_3CHClCOO)_2Cu$ and imidazole or substituted imidazole.

The following compounds were obtained:

A $(CH_3CHClCOO)_2Cu(\text{imidazole})_2$
A′ $(CH_2ClCH_2COO)_2Cu(\text{imidazole})_2$
B $(CH_3CHClCOO)_2Cu(\text{1-methylimidazole})_4(H_2O)_2$
B′ $(CH_2ClCH_2COO)_2Cu(\text{1-methylimidazole})_4(H_2O)_2$
C $(CH_3CHClCOO)_2Cu(\text{2-methylimidazole})_2(H_2O)_2$
C′ $(CH_2ClCH_2COO)_2Cu(\text{2-methylimidazole})_2(H_2O)_2$
D $(CH_3CHClCOO)_2Cu(\text{4-methylimidazole})_2(H_2O)_2$
D′ $(CH_2ClCH_2COO)_2Cu(\text{4-methylimidazole})_2(H_2O)_2$
E′ $(CH_2ClCH_2COO)_2Cu(\text{1,2-dimethylimidazole})_4(H_2O)_2$

The initial substances $(CH_3CHClCOO)_2Cu$ (compound O) and $(CH_2ClCH_2COO)_2Cu$ (compound O′) were also prepared.

Chemical analysis

The metal content was determined by EDTA titration. The 2- or 3-chloropropionate 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 inflection points: the first corresponding to the neutralization of imidazole or substituted imidazole, and the second corresponding to the neutralization of the 2- or 3-chloropropionate.

The results of quantitative elemental analysis for all the above-mentioned complexes 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 Setaram TG 85 microbalance.

The differential thermal analyses were performed on a Micro ATD M_4 using a heating rate of 4 K min^{-1}.

Thermoanalytical diagrams for the complexes are shown in Figs. 1 and 2. For all hydrated compounds, the initial temperature of decomposition was in the range 307–340 K; they all lost water molecules in one step, which appeared in DTA curves (Figs. 3 and 4) as an endothermic peak at that temperature. For the other complexes the initial decomposition temperature was around 470 K. Over a wide temperature range, the thermal decomposition of the studied compounds indicated small differences among them. The anions were evolved, as evidenced by a broad endothermic peak on the DTA

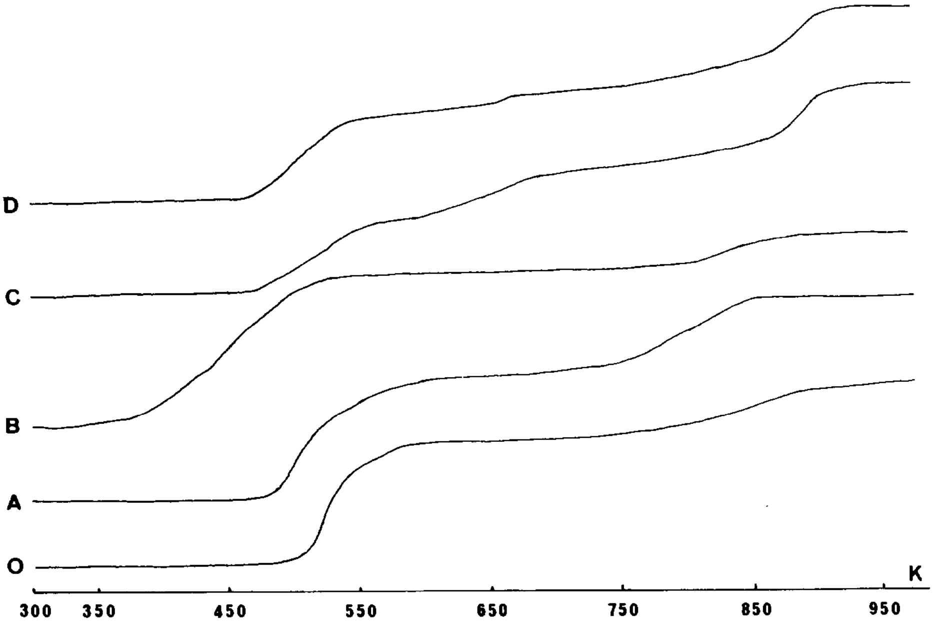

Fig. 1. TG curves in air (compounds O, A, B, C, D).

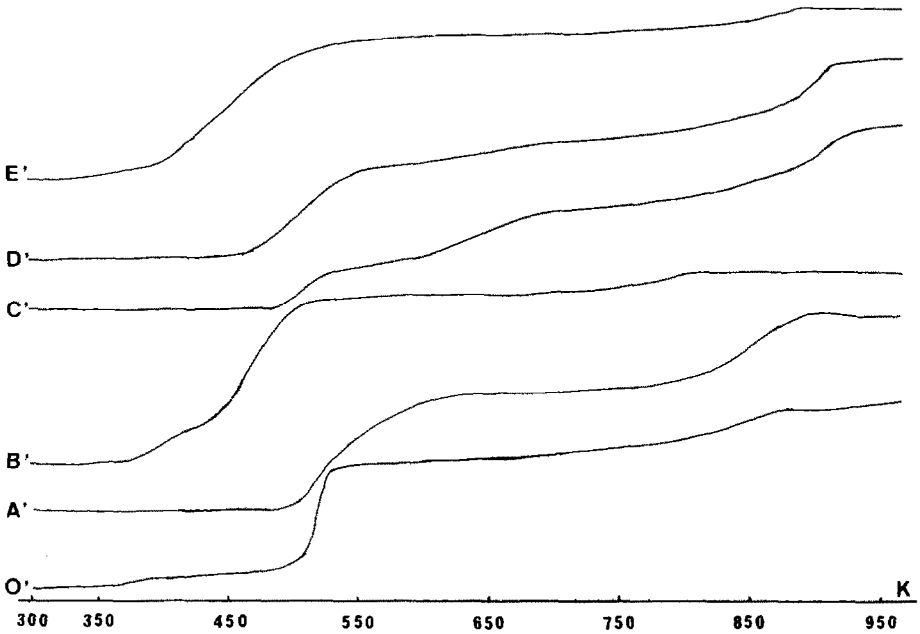

Fig. 2. TG curves in air (compounds O′, A′, B′, C′, D′, E′).

curve, but the reaction of loss of anions is not as simple as might be expected, since a clear exothermic peak was observed near 700–775 K with a shoulder on either side. This exothermic peak has been described by Melnik [10].

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

$$(CH_3CHClCOO)_2Cu(Imid)_2 \xrightarrow[\text{476–667 K}]{\substack{\text{W.L. \%theor. 51.82} \\ \text{W.L. \%exp. 52.10}}} [(CuImid)_2]$$

$$\xrightarrow[\text{667–831 K}]{\substack{\text{W.L. \%theor. 68.24} \\ \text{W.L. \%exp. 68.35}}} [Cu(Imid)]$$

$$\xrightarrow[\text{831–960 K}]{\substack{\text{W.L. \%theor. (if CuO only) 80.71} \\ \text{W.L. \%exp. 88.65}}} CuO + Cu^0$$

$$(CH_2ClCH_2COO)_2Cu(Imid)_2 \xrightarrow[\text{466–625 K}]{\substack{\text{W.L. \%theor. 51.87} \\ \text{W.L. \%exp. 52.69}}} [(CuImid)_2]$$

$$\xrightarrow[\text{625–830 K}]{\substack{\text{W.L. \%theor. 68.24} \\ \text{W.L. \%exp. 68.61}}} [Cu(Imid)]$$

$$\xrightarrow[\text{831–890 K}]{\substack{\text{W.L. \%theor. (if CuO only) 80.71} \\ \text{W.L. \%exp. 91.9}}} CuO + Cu^0$$

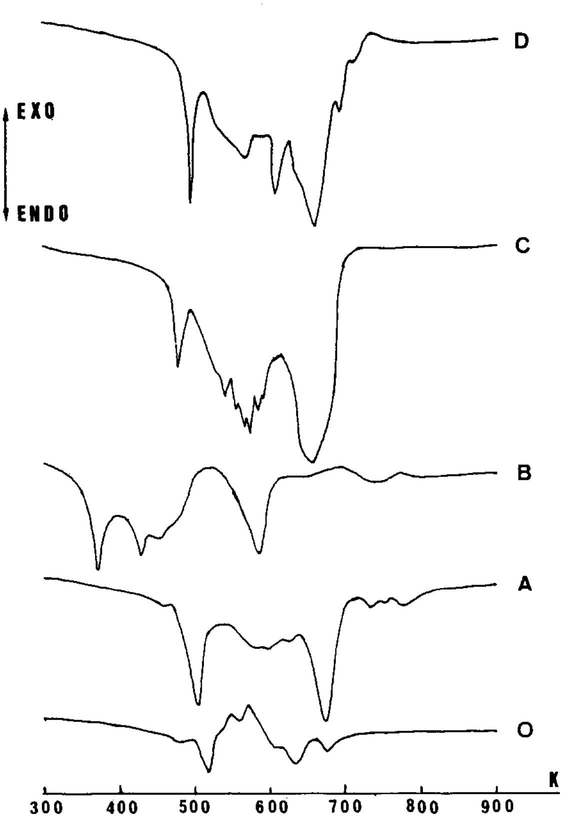

Fig. 3. Differential thermal curves in air (compounds O, A, B, C, D).

$(CH_3CHClCOO)_2Cu(1\text{-meImid})_4(H_2O)_2$

$$\xrightarrow[\text{307–414 K}]{\substack{\text{W.L. \%theor. 18.36}\\ \text{W.L. \%exp. 17.54}}} (CH_3CHClCOO)_2Cu(1\text{-meImid})_3$$

$$\xrightarrow[\text{414–802 K}]{\substack{\text{W.L. \%theor. 77.34}\\ \text{W.L. \%exp. 76.15}}} Cu(1\text{-meImid}) \xrightarrow[\text{802–930 K}]{\substack{\text{W.L. \%theor. 87.62}\\ \text{W.L. \%exp. 88.24}}} CuO$$

$(CH_2ClCH_2COO)_2Cu(1\text{-meImid})_4(H_2O)_2$

$$\xrightarrow[\text{314–380 K}]{\substack{\text{W.L. \%theor. 5.60}\\ \text{W.L. \%exp. 4.64}}} [(CH_2ClCH_2COO)_2Cu(1\text{-meImid})_4]$$

$$\xrightarrow[\text{380–407 K}]{\substack{\text{W.L. \%theor. 15.56}\\ \text{W.L. \%exp. 15.62}}} [(CH_2ClCH_2COO)_2Cu(1\text{-meImid})_3]$$

$$\xrightarrow[\text{407–660 K}]{\substack{\text{W.L. \%theor. 77.35}\\ \text{W.L. \%exp. 76.80}}} [Cu(1\text{-meImid})] \xrightarrow[\text{660–963 K}]{\substack{\text{W.L. \%theor. 87.62}\\ \text{W.L. \%exp. 87.78}}} CuO$$

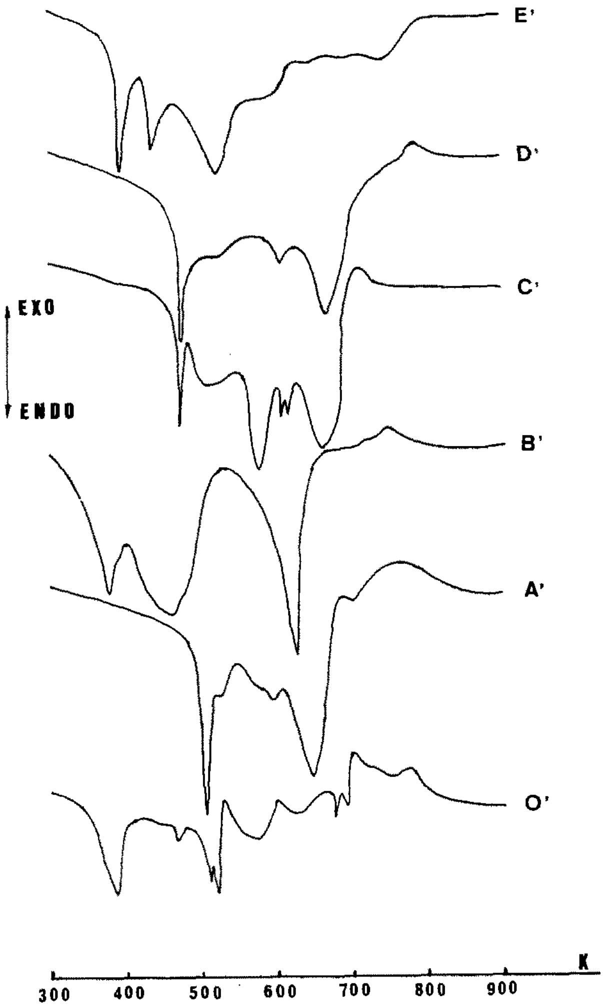

Fig. 4. Differential thermal curves in air (compounds O′, A′, B′, C′, D′, E′).

$$(\mathrm{CH_3CHClCOO})_2\mathrm{Cu(2\text{-}meImid)_2(H_2O)_2} \xrightarrow[\text{340–714 K}]{\substack{\text{W.L. \%theor. 52.45}\\ \text{W.L. \%exp. 53.25}}} [\mathrm{Cu(2\text{-}meImid)_2}]$$

$$\xrightarrow[\text{714–850 K}]{\substack{\text{W.L. \%theor. (if CuO only) 83.37}\\ \text{W.L. \%exp. 90.40}}} \mathrm{CuO + Cu^0}$$

$$(\mathrm{CH_2ClCH_2COO})_2\mathrm{Cu(2\text{-}meImid)_2(H_2O)_2}$$

$$\xrightarrow[\text{307–339 K}]{\substack{\text{W.L. \%theor. 7.52}\\ \text{W.L. \%exp. 7.71}}} [(\mathrm{CH_2ClCH_2COO})_2\mathrm{Cu(2\text{-}meImid)_2}]$$

$$\xrightarrow[\text{339–413 K}]{\substack{\text{W.L. \%theor. 52.45}\\ \text{W.L. \%exp. 51.29}}} [\mathrm{Cu(2\text{-}meImid)_2}] \xrightarrow[\text{413–540 K}]{\substack{\text{W.L. \%theor. 69.58}\\ \text{W.L. \%exp. 69.42}}} [\mathrm{Cu(2\text{-}meImid)}]$$

$$\xrightarrow[\text{540– 985 K}]{\substack{\text{W.L. \%theor. (if CuO only) 83.3}\\ \text{W.L. \%exp. 93.1}}} \mathrm{CuO + Cu^0}$$

$$(CH_3CHClCOO)_2Cu(4\text{-meImid})_2(H_2O)_2 \xrightarrow[452\text{–}680\ \mathrm{K}]{\substack{\text{W.L. \%theor. 52.45} \\ \text{W.L. \%exp. 52.89}}} [Cu(4\text{-meImid})_2]$$

$$\xrightarrow[680\text{–}945\ \mathrm{K}]{\substack{\text{W.L. \%theor. (if CuO only) 83.37} \\ \text{W.L. \%exp. > 90}}} CuO + Cu^0$$

$$(CH_2ClCH_2COO)_2Cu(4\text{-meImid})_2(H_2O)_2 \xrightarrow[344\text{–}719\ \mathrm{K}]{\substack{\text{W.L. \%theor. 52.45} \\ \text{W.L. \%exp. 51.69}}} [Cu(4\text{-meImid})_2]$$

$$\xrightarrow[720\text{–}945\ \mathrm{K}]{\substack{\text{W.L. \%theor. (if CuO only) 83.37} \\ \text{W.L. \%exp. 87.28}}} CuO + Cu^0$$

$$(CH_2ClCH_2COO)_2Cu(1,2\text{-dimImid})_4(H_2O)_2$$

$$\xrightarrow[308\text{–}398\ \mathrm{K}]{\substack{\text{W.L. \%theor. 8.19} \\ \text{W.L. \%exp. 8.12}}} [CH_2ClCH_2COO)_2Cu(1,2\text{-dimImid})_3]$$

$$\xrightarrow[398\text{–}786\ \mathrm{K}]{\substack{\text{W.L. \%theor. 78.76} \\ \text{W.L. \%exp. 76.47}}} [Cu(1,2\text{-dimImid})] \xrightarrow[786\text{–}830\ \mathrm{K}]{\substack{\text{W.L. \%theor. 89.11} \\ \text{W.L. \%exp. 89.71}}} CuO$$

SPECTRAL STUDIES

Electron paramagnetic resonance

The X-band first derivative ESR spectra were recorded for the powdered samples at room temperature and in liquid nitrogen at 77 K with a Varian V 4500A spectrometer equipped with a dual cavity. Strong pitch Varian was used as a reference for g determination ($g_{sp} = 2.0028$).

Sample O′ (Fig. 5) exhibits at room temperature the ESR spectrum expected for dimeric copper complexes with large D values, such as copper acetate monohydrate ($D \approx 30\ \mathrm{m}^{-1}$) [11]. In such cases the positions of ESR lines in the powder spectrum, H_1, H_2 and H_3, can be calculated according to the following relation

$$h_\nu = |D| - g_\parallel \beta H_1$$

$$h_\nu = -|D| + g_\parallel \beta H_2$$

$$h_\nu = -\frac{|D|}{2} + \left(\frac{D^2}{4} + g_\perp^2 \beta^2 H_3^2\right)\frac{1}{2}$$

The ESR spectrum recorded with sample O at room temperature is much more difficult to interpret. It results from the superimposition of lines coming from three species, as evidenced by (1) a wide line centred around 2.18 (unknown species), (2) a narrow line at 2.178 (monomer species) and (3) three lines, H_1, H_2 and H_3, assigned to a triplet state coming from a copper dimer. Because of this superimposition it is difficult to give accurate values for the g and D parameters (Table 1).

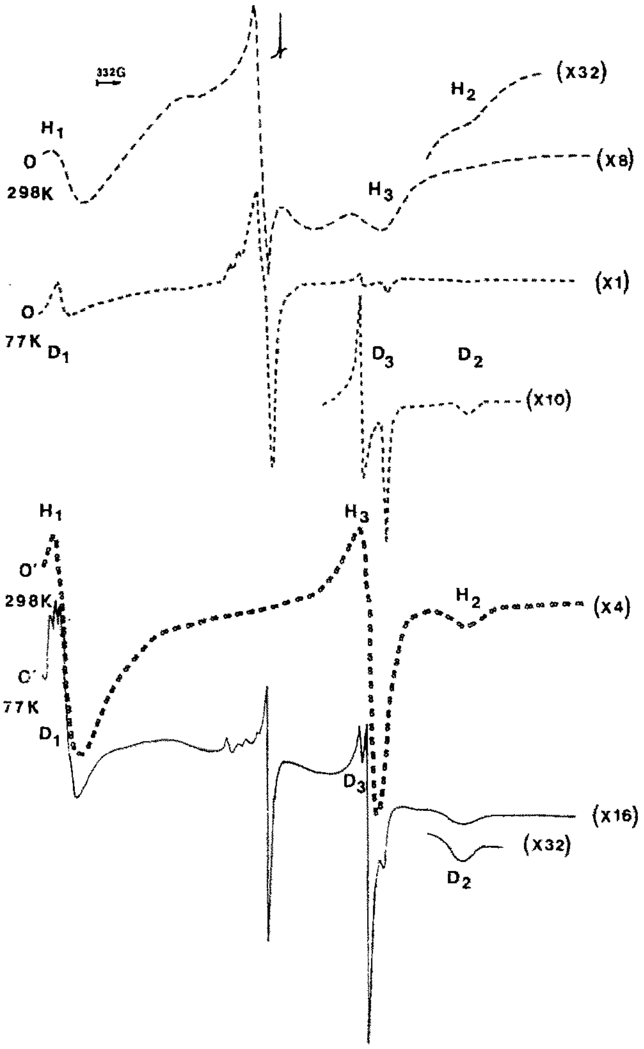

Fig. 5. ESR spectra of compounds O and O′ at 298 K and 77 K.

At low temperature the asymmetrical line due to monomeric copper species develops clearly. In the case of sample O this part of the spectrum cannot be interpreted using a single copper complex. The relative intensity decrease of the other lines (D_1, D_2, D_3) is in agreement with a thermally accessible triplet state. The seven-line hyperfine structure of the D_1 line characteristic of such copper dimers is observed for sample O′ only.

The splitting of the D_3 line for sample O shows that we have to consider an E term in the spin hamiltonian, and the values of g_x, g_y, g_z, D and E can be calculated using the formula given by Sharrock et al. [12]. A further hypothesis is necessary to complete the calculations: the g anisotropy is

TABLE 1

ESR parameters of initial compounds

Parameter	Compound O		Compound O′		
	298 K	77 K	298 K	77 K	
Monomer					
$g_{\parallel}$	2.35_6	2.35_9	–	2.27_6	
$g_{\perp}$	2.04_8	2.04_4	–	2.04	
$a_{\parallel}$ (gauss)	–	125	–	150	
Dimer					
H_1 (gauss)	427	327	377	297	
$a_{\parallel}$ (gauss)	–	–	–	64	
H_2 (gauss)	5993	5927	5927	5926	
H_3 (gauss)	4670	4460 4826	4593	4635	
$g_{\parallel}$	2.38_2	–	2.38_9	2.35_5	
$g_{\perp}$	2.04_3	–	2.10_9	2.07_5	
D (m^{-1})	35.70		35.15	O'_1 34.21	O'_2 27.11
$E' = \frac{E}{g_0 \beta}$ (gauss)		101		95	–

sufficiently small to consider in first approximation that $g_x \simeq g_y = g_{\perp}$. The obtained values of $g_{\perp}$, $g_{\parallel}$, D and E are given in Table 1.

To complete the interpretation of spectrum O′ at 77 K we must consider two dimers. A first one, O'_1, with complete crystal field asymmetry and interpreted as the one described for sample O at 77 K, and a second one, O'_2, with axial crystal field symmetry (Table 1).

TABLE 2

ESR parameters of different complexes

Compound	$g_{\perp}$ 298 K	$g_{\parallel}$ 298 K	$\bar{g}$ 298 K	$a_{\parallel}$ 298 K (gauss)	$g_{\perp}$ 77 K	$g_{\parallel}$ 77 K	$\bar{g}$ 77 K	$a_{\parallel}$ 77 K (gauss)	Purity
A	2.03_9	2.15_8	2.08_6		2.03	2.16	2.09_2		Monomer
B	2.01_6	2.27	2.06_7	166	2.02_3	2.28_4	2.06_7	165	Pure monomer
C	2.06	(2.41_6)	2.06_5						
D	2.03	(2.43)	2.05		2.03	(2.43_6)	2.06		
A′	2.03	2.15	2.08_7		2.03_8	2.16	2.08_6		Monomer
B′	2.01_7	2.27_6	2.06_5	157	2.02_3	2.28_4	2.06_7	165	Pure monomer
C′	2.05	(2.36_5)	2.06_5		2.04_4	–	2.08_6		
D′	2.03_3	(2.46)	2.06_5		2.02_8	(2.47_6)	2.05_4		
E′	2.03_3	(2.46)	2.06_5		2.03_3	2.46	2.06_5		

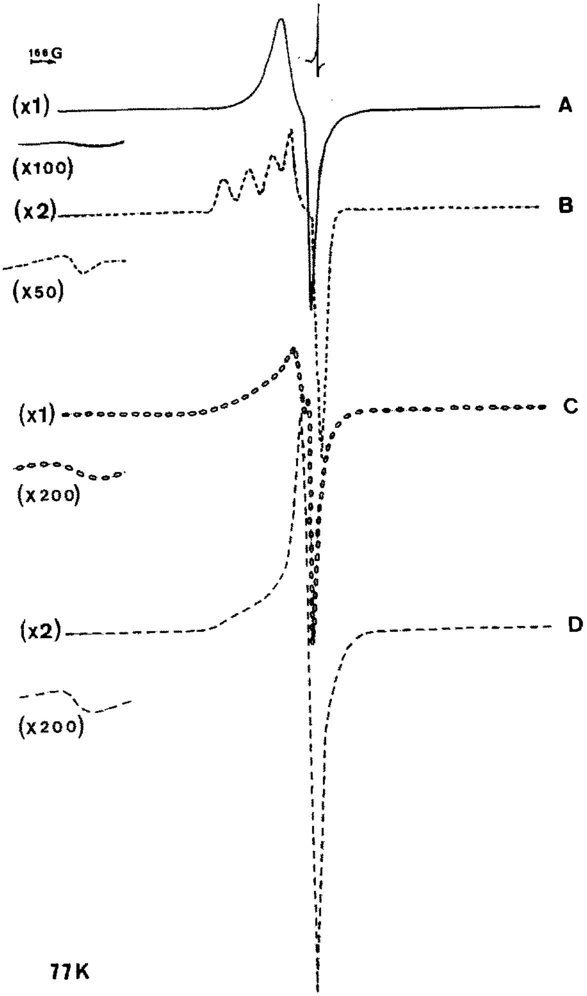

Fig. 6. ESR spectra of compounds, A, B, C and D at 77 K.

All complexes obtained after reactions with the different imidazole molecules exhibit a more or less symmetrical ESR line generally assigned to mononuclear copper species. In the case of such species ($S = \frac{1}{2}$) with axial symmetry the g values are taken at the extrema of the derivative. For a nearly symmetrical line, the mean g value ($\bar{g}$) has been measured at the zero point of the derivative. The temperature does not affect the shape of the signal. We only observed the expected increase in intensity at low temperature. The spectra recorded at 77 K are shown in Figs. 6 and 7. The hyperfine structure of the parallel part of the ESR signal is well defined for copper chloropropionates reacted with 1-methylimidazole. For imidazole and 2-methylimidazole the hyperfine structure is not resolved, but the shape of the spectrum clearly indicates two g values, tentatively assigned to $g_\perp$ and $g_\parallel$ in Table 2. Concerning the 2-methylimidazole, 4-methylimidazole and 1,2-di-

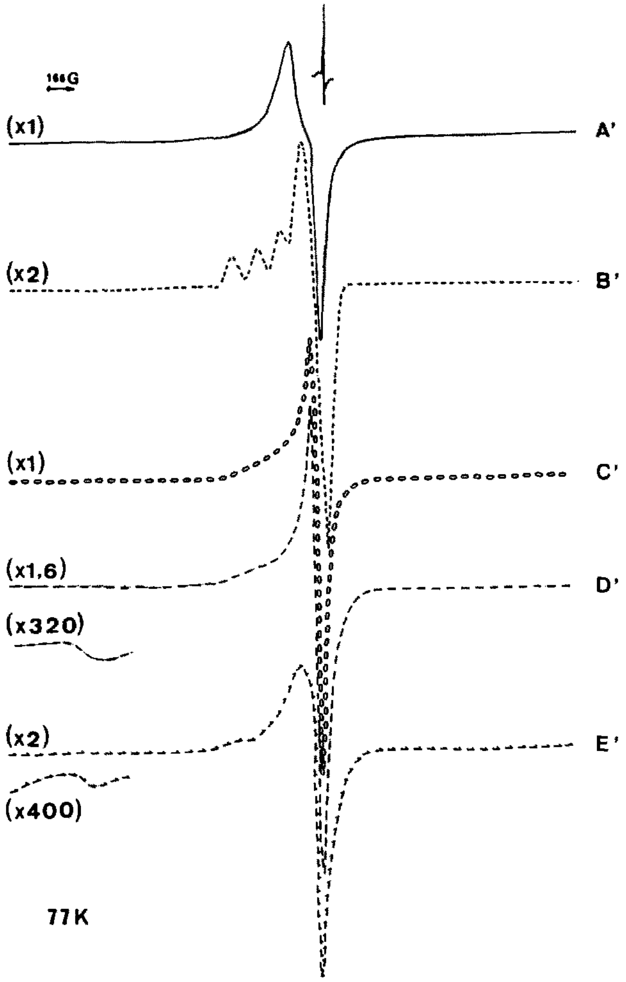

Fig. 7. ESR spectra of compounds, A′, B′, C′, D′ and E′ at 77 K.

methylimidazole complexes, we give only a mean g value. The small shoulder at an apparent g value of 2.45, and given in parentheses in Table 2, could be interpreted as an ill-defined $g_{\parallel}$ band. However, it is also possible to assign such a line to dimeric species. The $\Delta_{\mathrm{ms}} = 2$ line at high amplification would confirm such an interpretation. Considering species with small D values, and interpretation according to Chikira and Kon [13] with superposition of central lines, we can deduce the following approximate values

Compound C: $D = 1.12\ \mathrm{m}^{-1}$ $g_{\parallel} = 2.22$
Compound C′: $D = 1.01\ \mathrm{m}^{-1}$ $g_{\parallel} = 2.14$
Compound D: $D = 1.05\ \mathrm{m}^{-1}$ $g_{\parallel} = 2.15$
Compound D′: $D = 1.32\ \mathrm{m}^{-1}$ $g_{\parallel} = 2.23$
Compound E′: $D = 1.28\ \mathrm{m}^{-1}$ $g_{\parallel} = 2.23$

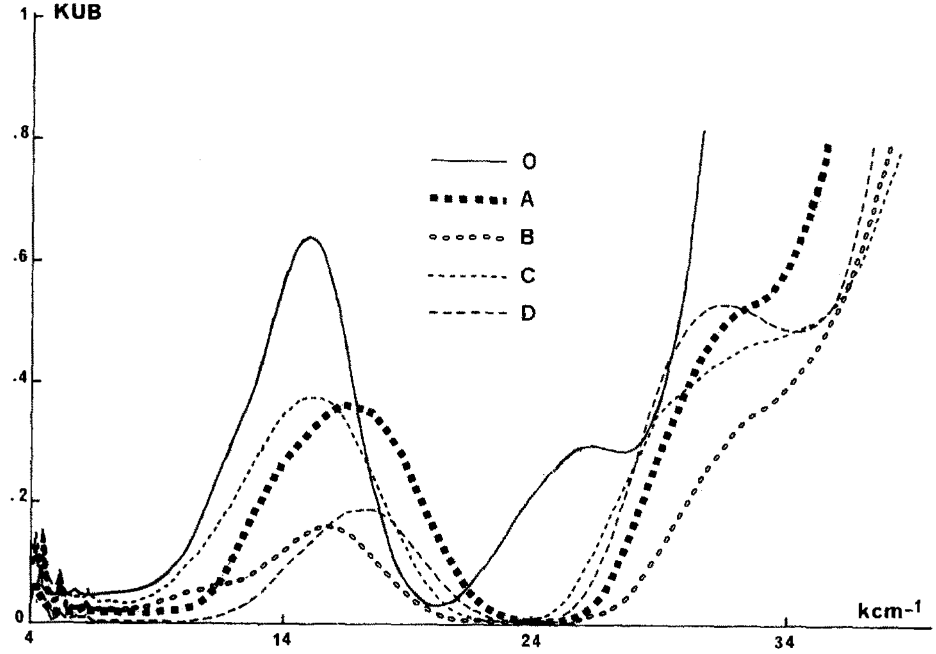

Fig. 8. Reflectance spectra (compounds O, A, B, C, D).

Diffuse reflectance spectra

Diffuse reflectance spectra (Figs. 8 and 9) were recorded at room temperature for all compounds using a Beckman UV 5240 spectrometer equipped

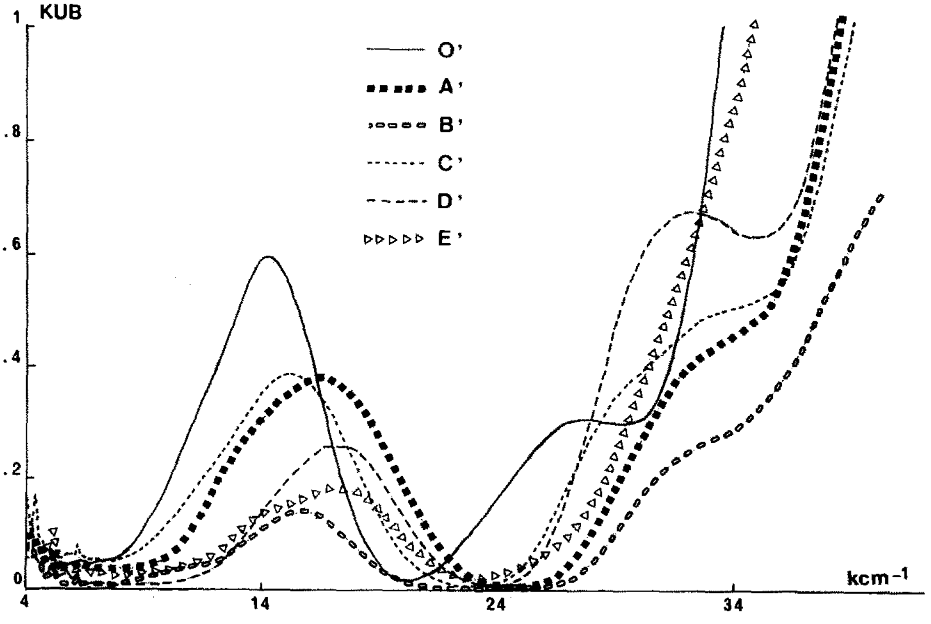

Fig. 9. Reflectance spectra (compounds O′, A′, B′, C′, D′, E′).

TABLE 3

Reflectance: ΔE_{max} values

Compound	ΔE_{max}	Compound	ΔE_{max}
O	14990	O′	14315
	25984		25875
A	16540	A′	16630
	17330		
	31060		31313
B	11715	B′	10390
	15773		15760
	31535		31300
C	15225	C′	15200
	29555		29550
D	16600	D′	16610
	17600		17450
	30600		30270
		E′	14325
			16675
			31740

with an integration sphere. In the range 4000–40000 cm^{-1}, Kodak white reflectance was used as a standard and for the dilution of the copper complexes (10 wt%). For the compounds O and O′ (see Table 3), in which copper pairs are evidenced by ESR, we observed three absorption bands at around 15000, 26000 and 40000 cm^{-1}. The first band arises from a ligand field transition and the third we assigned to a charge transfer absorption. Concerning the band at 26000 cm^{-1}, its attribution differs according to the authors [14–17], but it is often assigned to a simultaneous pair excitation of a d–d transition by a photon of about twice the energy of the simple (d–d) transition [18,19]; such a band is missing in all the imidazole chloropropionate complexes. The band at 30000 cm^{-1} can be associated with an absorption of the imidazole ligand. The shift towards lower wavenumber of this band is due to modification of the energy level of the molecule linked to the Cu^{2+} ion.

CONCLUSION

ESR results show that the chlorocarboxylates used as starting material do not exhibit the same behaviour. Moreover, it seems that at least two paramagnetic copper species (isolated copper ions and copper pairs) contribute to give the observed spectra. After complexation with imidazole compounds it is impossible to differentiate 2- and 3-chloropropionate complexes. We do not observe strong coupling between copper ions, and reflectance spectra confirm this observation.

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