Thermochimica Acta, 194 (1992) 265–274
Elsevier Science Publishers B.V., Amsterdam

Study of copper(II) malates complexed with imidazole or methyl substituted imidazoles

A. Busnot [a], J. Masson [a], J.F. Hemidy [b] and J.F. Le Querler [a]

[a] *Laboratoire de Chimie Minérale et Bioinorganique, U.F.R. de Sciences, Université de Caen, Esplanade de la Paix, 14032 Caen Cedex (France)*
[b] *Laboratoire de Structures et Réactivité d'espèces absorbées, ISMRA, U.R.A. 4, Université de Caen, 14050 Caen Cedex (France)*

(Received 24 April 1991)

Abstract

The preparation of new complexes involving copper(II) malate and imidazole or methyl-substituted imidazoles is described. The results of thermal and spectral studies are analysed for the various complexes. The TGA curves and ESR and diffuse reflectance spectra are reported. The monomeric character of the different complexes is shown.

INTRODUCTION

Binding between metal(II) ions and imidazole ligands occurs frequently in nature, as many metallo-proteins are coordinated by the imidazole side chains of histidyl residues. Metal coordination compounds containing imidazole ligands have been synthesised for many years and have been studied intensively, both structurally and spectroscopically [1–4]. So far the number of thermochemical investigations on imidazole compounds has been limited [5–8].

In a previous work [9], we studied several Cu(II) complexes in which the metallic ion is mixed–ligated with a succinate dianion and two imidazoles or methyl-substituted imidazoles. The interest of the malate ion is that it introduces an asymmetric C atom into the molecule.

The preparation of these compounds and their analytical and spectral data are given and discussed below.

PREPARATION

Five complexes involving Cu(II) malate and imidazole or substituted imidazole were prepared (Table 1): A, malate Cu(imidazole)$_2$; B, malate Cu(1-methylimidazole)$_2 \cdot (H_2O)_2$; C, malate Cu(2-methylimidazole)$_2$; D, malate Cu(4-methylimidazole)$_2$; and E, malate Cu(1,2-dimethylimidazole)$_2$.

TABLE 1

Microanalysis results

Compound	Element	Theoretical (%)	Experimental (%)
Cu(malate)(Imid)$_2$ (A)	C	36.20	36.10
	H	3.64	3.42
	N	16.88	17.09
	Cu	19.15	19.44
Cu(malate)(1-MeImid)$_2$(H$_2$O)$_2$ (B)	C	38.14	38.25
	H	4.76	4.84
	N	14.83	14.85
	Cu	16.82	16.95
Cu(malate)(2-MeImid)$_2$ (C)	C	40.06	41.04
	H	4.45	4.62
	N	15.57	15.48
	Cu	17.65	17.38
Cu(malate)(4-MeImid)$_2$ (D)	C	40.06	40.57
	H	4.45	4.35
	N	15.57	15.77
	Cu	17.65	17.66
Cu(malate)(1,2-diMeImid)$_2$ (E)	C	43.35	43.31
	H	5.16	5.30
	N	14.44	14.41
	Cu	16.38	16.17

The starting material, Cu(OCO–CHOH–CH$_2$–COO) (compound O), was also prepared. A mixture of malic acid, $CuCO_3 \cdot Cu(OH)_2 \cdot nH_2O$ and imidazole or substituted imidazole was heated with magnetic stirring in 100 cm^3 of ethanol–water (75/25). The mixture was allowed to reflux for one hour, and then the hot mixture was filtered. The blue solution obtained was left for crystallisation (compounds A and D) or desiccation in air (B, C and E).

For compound B, the best result was obtained using the following method: a mixture of Cu(II) malate $\cdot nH_2O$ (prepared in our laboratory) and 1-methylimidazole was heated in 50 cm^3 of water with magnetic stirring and allowed to reflux for one hour. The hot solution was filtered, then left for desiccation. Both methods for this complex yielded a blue-green powder, but the analysis showed that the one obtained with the second method was more homogeneous. In any case, compound B is hygroscopic and less stable than the others. Compounds A, C, D and E could not be obtained using this second procedure.

THERMAL STUDIES

Additional studies were carried out by thermogravimetry to confirm the molecular formulae assumed on the basis of elemental analysis and to

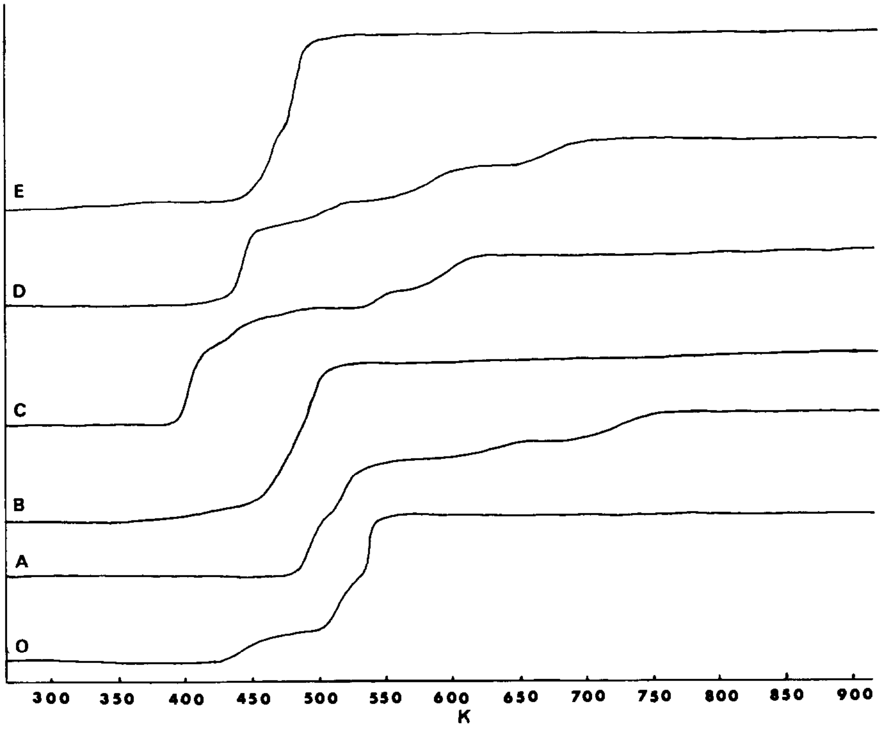

Fig. 1. TG curves in air.

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 analysis was performed on a micro A.T.D. M4 using a heating rate of 4 K min^{-1}.

Thermoanalytical diagrams for the complexes are shown in Figs. 1 and 2. The thermal decomposition curves for complexes A, C and D and for complexes B and E are similar. For complex B, the TGA curves show a first-step decomposition from 440 to 730 K (weight loss, 78.7%) with a small inflection at 500 K (weight loss 35%). The shape of the curve seems to indicate the loss of a small amount of water during the early stage of the decomposition (the amount being very difficult to assess). On the DTA curve, there is an endothermic peak at 425 K and an exothermic signal near 730 K. Between these two peaks, the curve is irregular due to the decomposition of the product. A similar type of curve was observed for complex E; an endothermic step at about 460 K confirms the loss of one ligand molecule. Over a wide temperature range the DTA diagrams indicate small differences between all the complexes studied.

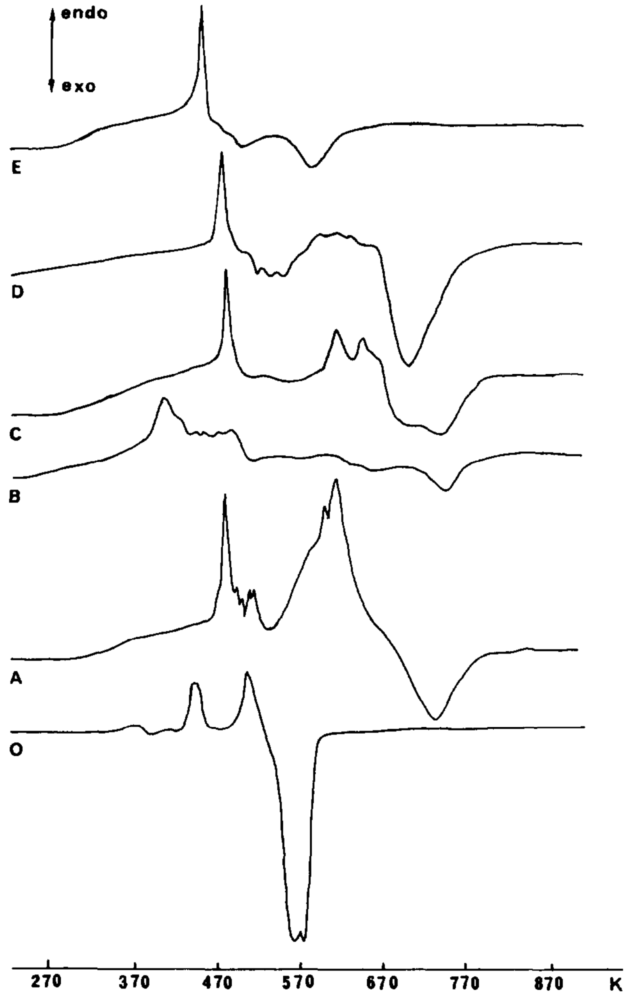

Fig. 2. Thermal differential curves in air.

The general decomposition scheme of the different complexes can be summarised in the mechanisms

$$\text{compound A} \xrightarrow[470\text{–}510\ \text{K}]{\substack{\text{wt. loss: Th, 20.5\%} \\ \text{Exp, 23.36\%}}} [\text{malate Cu(Imid)}] \xrightarrow[510\text{–}540\ \text{K}]{\substack{\text{wt. loss: Th, 41.02\%} \\ \text{Exp, 46.7\%}}}$$

$$[\text{malate Cu}] \xrightarrow[540\text{–}774\ \text{K}]{\substack{\text{wt. loss: Th, 76.01\%} \\ \text{Exp, 75.54\%}}} \text{CuO}$$

$$\text{compound B} \xrightarrow[355\text{–}459\ \text{K}]{\substack{\text{wt. loss: Th, 8.13\%} \\ \text{Exp, 9.02\%}}} [\text{malate Cu(1-MeImid)}_2] \xrightarrow[459\text{–}730\ \text{K}]{\substack{\text{wt. loss: Th, 79.79\%} \\ \text{Exp, 78.61\%}}} \text{CuO}$$

$$\text{compound C} \xrightarrow[386\text{–}456\ \text{K}]{\substack{\text{wt. loss: Th, 45.86\%} \\ \text{Exp, 44.64\%}}} [\text{malate Cu}] \xrightarrow[456\text{–}830\ \text{K}]{\substack{\text{wt. loss: Th, 77.87\%} \\ \text{Exp, 77.41\%}}} \text{CuO}$$

$$\text{compound D}\xrightarrow[394\text{–}534\ \text{K}]{\substack{\text{wt. loss: Th, }46.38\%\\ \text{Exp, }45.86\%}}[\text{malate Cu}]\xrightarrow[534\text{–}727\ \text{K}]{\substack{\text{wt. loss: Th, }77.75\%\\ \text{Exp, }78.48\%}}\text{CuO}$$

$$\text{compound E}\xrightarrow[315\text{–}485\ \text{K}]{\substack{\text{wt. loss: Th, }24.77\%\\ \text{Exp, }24.23\%}}[\text{malate Cu(1,2-diMeImid)}]$$

$$\xrightarrow[485\text{–}831\ \text{K}]{\substack{\text{wt. loss: Th, }80.29\%\\ \text{Exp, }80.79\%}}\text{CuO}$$

The compounds in brackets were assumed but not isolated.

For complex A, the DTA curves show endothermic peaks at 480 K and 531 K and a large exothermic signal at about 750 K. The irregular aspect of the curve between the two endothermic peaks confirms the decomposition that occurs in this range of temperature. For the other complexes with the same decomposition scheme, an exothermic signal appears near 700–750 K associated with the decomposition of the complexes. An endothermic peak occurs when the ligand is lost from the complexes.

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, using a Varian V4500A spectrometer equipped with a dual cavity. Strong pitch Varian was used as a reference for g determination (2.0028).

Samples O, A, C, D and E (Figs. 3 and 4) exhibit the ESR spectra expected for monomeric copper complexes at both temperatures. Orthorhombic symmetry characterized by three g values (Table 2) for complexes O, A, C and E, and axial symmetry for complex E, were observed.

Hyperfine structure was not observed because of magnetic interaction between neighbouring copper ions. For compound B, the shape of the ESR line is affected by the temperature. In addition to a nearly symmetrical line centred at $g = 2.11$, a shoulder at $g_{\text{ap}} = 2.51$ can be clearly seen at room temperature; and using higher amplification, the $\Delta_{\text{ms}} = 2$ line develops in the low-field part of the spectrum. A lowering of the temperature results in a nearly complete disappearance of the shoulder. A g_{ap} valued of around 2.50 is too high to be assigned to the parallel part of an anisotropic signal. We therefore believe that in complex B, interactions between copper ions are strong enough to prevent the observation of monomeric copper spectra. Such an interpretation has already been suggested in the case of copper chloropropionate complexes [10]. The structural differences giving rise to these interactions supports the different behaviour observed for complex B in the thermogravimetric analysis and seems to be related to the presence of a methyl group in position 1 of the imidazole ring.

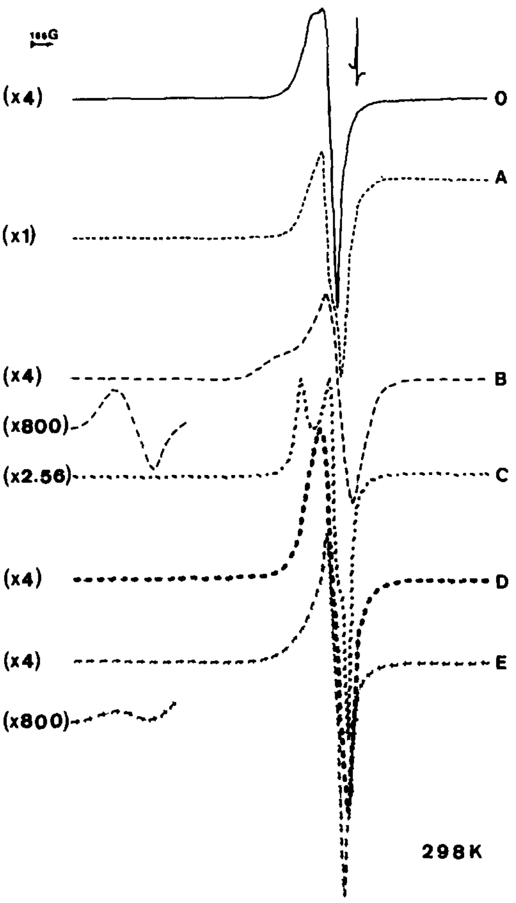

Fig. 3. ESR of compounds at 298 K.

Diffuse reflectance spectra

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

Sample O exhibits a nearly symmetrical absorption band at 14 000 cm^{-1}. The asymmetric band observed for all other samples results apparently from the superimposition of two overlapping bands. The resolution of the two absorbtion bands (Table 3) can be associated with the lower value of $(g_3 - g_1)$ observed by ESR.

TABLE 2

ESR parameters of the different complexes

Compound	g 298 K	g 298 K	g_1 298 K	g_2 298 K	g_3 298 K	g 77 K	g 77 K	g_1 77 K	g_2 77 K	g_3 77 K
O			2.09^{2}	2.13^{7}	2.25			2.08^{9}	2.13^{7}	2.24
A			2.06^{3}	2.14^{7}	2.25 [a]			2.06^{2}	2.14^{7}	2.25 [a]
B	$\bar{g} = 2.10$							$\bar{g} = 2.11$		
C			2.04^{6}	2.11^{6}	2.30^{9}			2.06	2.10^{4}	2.30^{8}
D			2.05^{5}	2.14^{7}	[a]				2.14^{6}	2.25
E					2.07	2.31				

[a] Poorly defined.

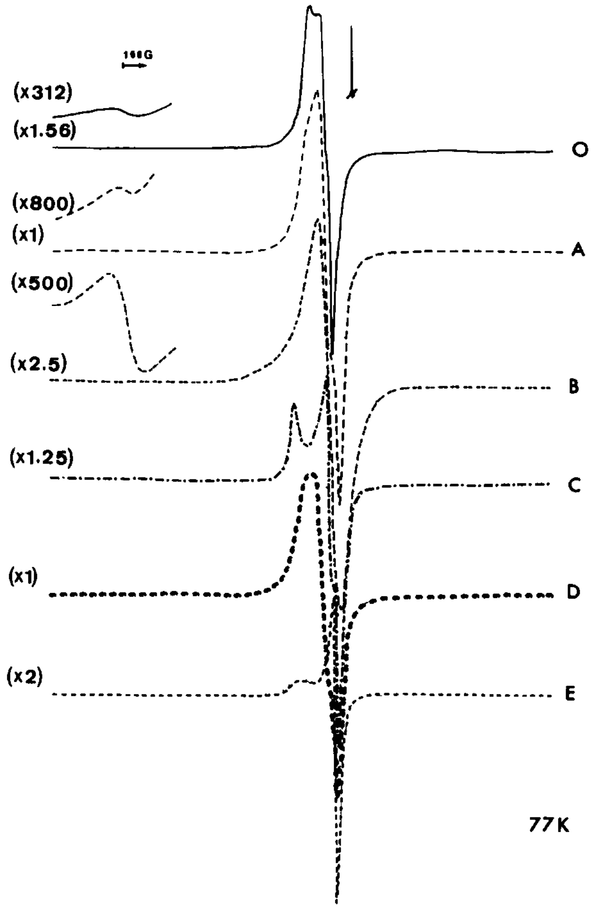

Fig. 4. ESR of compounds at 77 K.

An estimation of the covalency factors k_0^2 is possible using the mean g_0 value ($g_0 = (g_1 + g_2 + g_3)^3$) and the $\Delta E_{\max}$ value as the mean position of the two overlapping bands. The values given in Table 4 are close to those generally obtained [11,12].

TABLE 3

Reflectance parameters

Compound	$\Delta E_{\max}$ (cm^{-1})	Compound	$\Delta E_{\max}$ (cm^{-1})
O	14000	C	11300
A	10545		13920
	14270	D	11080
B	10453		14160
	14276	E	9705 (shoulder)
			14300

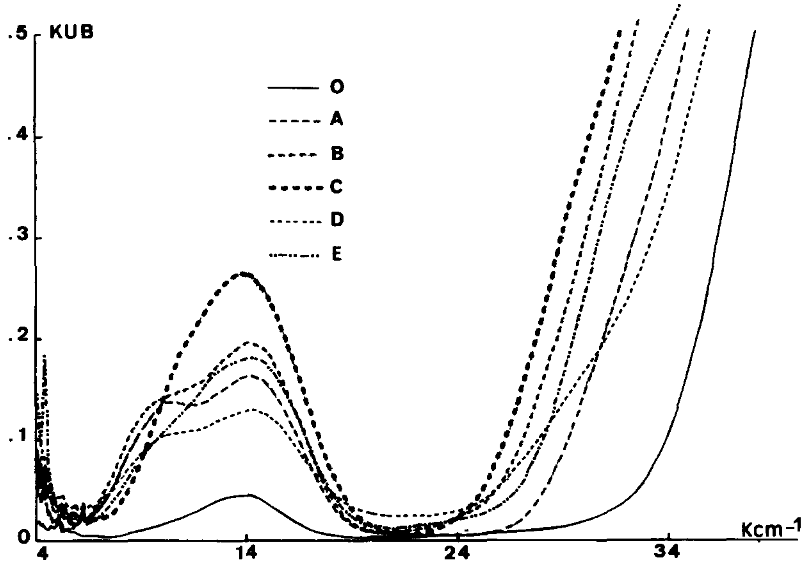

Fig. 5. Reflectance spectra.

TABLE 4

Covalency parameters k_0^2 of the different complexes

Compounds	g_m	ΔE_{max} (cm^{-1})	$k_0^2 = -\frac{\Delta E_{max}(g_m - 2)}{4\lambda}$ [a]
O	$g_m = 2.15^9$	14000	0.67
A	$g_m = 2.15^3$	12407	0.575
B	$g = 2.10$	12364	0.375
C	$g_m = 2.15^7$	12610	0.60
D	$g_m = 2.15$	12620	0.574
E	$g = 2.11$	12047	0.402

[a] $\lambda = -825$ cm^{-1}.

REFERENCES

1 J. Reedijk, Recl. Trav. Chim., 88 (1969) 145.

2 A. Santoro, A.D. Mighel, M. Zocchi and C.W. Reimann, Acta Crystallogr. Sect. B, 25 (1969) 84.

3 H.M.J. Hendriks and J. Reedijk, Recl. Trav. Chim., 98 (1979) 95.

4 J. Reedijk and G.C. Verschoor, Acta Crystallogr. Sect. B, 29 (1973) 721.

5 J.G. Van Berkum, G. Hakvoort and J. Reedijk, Thermochim. Acta, 43 (1981) 49.

6 J.C. Van Dam, G. Hakvoort, J.C. Jansen and J. Reedijk, J. Inorg. Nucl. Chem., 37 (1975) 713.

7 P.S. Gomm, A.E. Underhill and R.W.A. Oliver, J. Inorg. Nucl. Chem., 34 (1972) 1879.

8 M.C. Navarro Ramsinger and M. Gayoso Andrade, J. Therm. Anal., 14 (1978) 281.

9 J. Masson, A. Busnot, F. Busnot, J.F. Hemidy and J.F. Le Querler, Thermochim. Acta, 122 (1987) 221.

10 A. Busnot, F. Busnot, J.F. Hemidy and J.F. Le Querler, Thermochim. Acta, 179 (1991) 135.

11 M.A. Bernard, A. Busnot, F. Busnot and J.F. Le Querler, Thermochim. Acta, 146 (1989) 39.

12 H. Yokoi, M. Say, T. Isobe and S. Ohsaka, Bull. Chem. Soc. Jpn., 45 (1972) 2189.