Pyridine-type complexes of transition-metal halides XII. Solid-state studies of copper(II)-chloride and bromide complexes with methylpyridines. Part I: Complexes with 3-methylpyridine

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Abstract

The structural characteristics and thermal behaviour of the copper(II)-chloride and bromide complexes of 3-methylpyridine synthesised by a solid–gas phase technique are described. Far-IR spectra and results of the X-ray studies of the parent compounds and the intermediates indicate a host–guest phenomenon, a new structural feature of transition-metal halide complexes. © 1998 Elsevier Science B.V.

Keywords: Copper(II) halide–3-methylpyridine complexes; Host–guest phenomenon

1. Introduction

We have undertaken a broad study of transition-metal halide organo complexes, [1–4], and we now investigate complexes of copper(II) halides with methylpyridines, lutidines and 2,4,6-collidine. This paper reports the synthesis, spectral data and thermal properties of the chloro and bromo complexes of 3-methylpyridine. A novel host–guest phenomenon is apparent for these complexes. Spectroscopic and X-ray diffraction data also confirm the zeolitic property of these compounds.

The copper(II) chloride and bromide complexes of 3-methylpyridine were obtained by a solid–gas phase technique and the thermal intermediates were isolated at the appropriate temperatures, as indicated by thermal analysis studies.

2. Experimental

2.1. Preparation

All chemicals used were of analytical reagent grade. The crystalline copper(II) chloride and bromide complexes with 3-methylpyridine were obtained by a solid–gas phase preparation method. The appropriate

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copper(II) halide was placed in a desiccator saturated with 3-methylpyridine vapour at room temperature. The course of the reaction was monitored by measuring the mass change of the copper(II) halide until no further increase was detected. After a maximum copper(II)-to-ligand ratio of 1 : 4.2, some decrease in mass occurred for both the chloride and bromide complexes.

The intermediates were isolated at the appropriate temperatures as indicated by the corresponding TG-DTG curves.

2.2. Analyses

The hydrogen, carbon and nitrogen contents of the complexes were determined using a Carlo Erba elemental analyser.

The electronic spectra were obtained using a Beckmann Acta MIV spectrophotometer.

The far-IR (FIR) spectra (500–30 cm^{-1}) were recorded using a BIO-RAD Digilab FTS-40 system. FT-FIR measurements were performed in the solid state, in polyethylene pellets and in Nujol mulls at 4 cm^{-1} resolution with co-addition of 512 scans for each spectra.

TG data were obtained using a DuPont-1090 TA system. The DSC measurements were carried out using an open aluminium pan as sample holder and an empty aluminium pan as reference. The chloride complex was heated at a rate of 5 K min^{-1} in the flowing air and argon atmospheres over a heating range from room temperature to 600 K. As the two decomposition curves were identical, all other measurements were carried out at a heating rate of 5 K min^{-1} in an air atmosphere. The sample masses were ca. 5 mg.

The unit-cell parameters for the complexes were obtained by X-ray powder diffraction using a Guinier–Hägg focussing camera with Cu $K_{\alpha 1}$ radiation and photographic recording. Silicon (a=5.430 880 Å) was added as an internal standard, and used for the refinement of the unit-cell dimensions. The film strips were measured with an automatic optical reader [5] yielding relative line intensities and geometrical positions. The powder diffraction characteristics were further evaluated with TREOR 90, a trial-and-error indexing programme [6,7].

3. Results and discussion

The elemental analysis data for the intermediates are shown in Table 1 and these agree with the stoichiometries $Cu(L)_2X_2$ (where X=halogen and L= 3-methylpyridine). As the composition of the labile parent compounds depends on time, the results for their elemental analysis are not presented.

The far-IR spectra of the intermediates verify the coordination of copper(II) to the ligand [8]. The observed frequencies are listed in Table 2. The parent compounds have different structures. Namely, in the case of the chloride complex, the presence of free, non-coordinated ligands can be observed (483, 454, 400, 353, and 220 cm^{-1}) [9] while in the spectrum of the bromide complex, both non-coordinated and bonded [10] (ν(CuBr)=246 and 209 cm^{-1}) 3-methylpyridine are evident.

The electronic spectral data of the complexes are presented in Table 3. The position of the bands suggests a $^2E_g \rightarrow {}^2T_{2g} d \rightarrow d$ transition in all cases, corresponding to a distorted octahedral environment for the copper(II) ion [11] in both the parent compounds and in the intermediates.

Table 1
Elemental analyses

Compound	%C		%H		%N	
	calc.	found	calc.	found	calc.	found
$Cu(L)_2Cl_2$	44.94	44.34	4.40	4.05	8.73	8.60
$Cu(L)_2Br_2$	35.19	34.34	3.44	3.35	6.84	6.52

Table 2
Far-IR data of the intermediates

Compound	ν(CuX)	νCuN)	Ligand bands
$Cu(L)_2Cl_2$	294vs	267s, 234w	485w, 414s, 360w, 212wm
$Cu(L)_2Br_2$	239vs	269s	497w, 484w, 414s, 358w

Table 3
Electronic spectra

Compound	$Cu(L)_4Cl_2$	$Cu(L)_2Cl_2$	$Cu(L)_4Br_2$	$Cu(L)_2Br_2$
Peak position (cm^{-1})	15.384	14.749	15.267	14.598
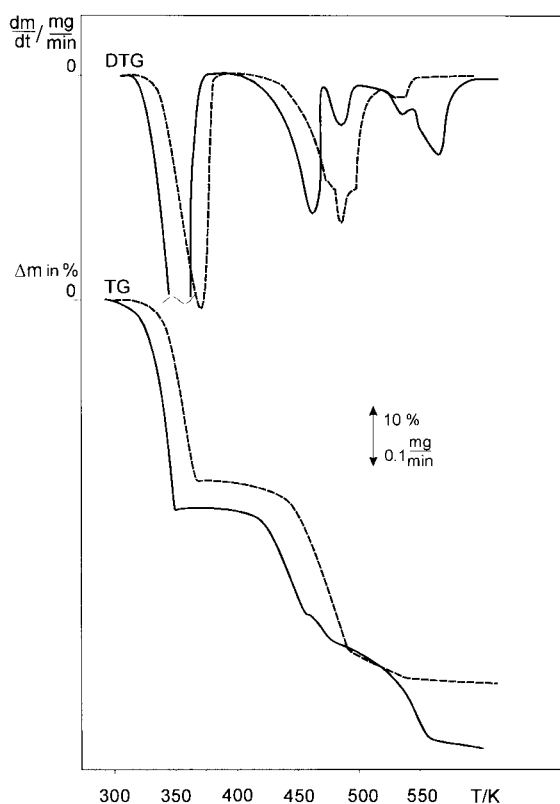
Fig. 1. TG and DTG curves of (———) $[Cu(L)_2Cl_2]$–L_n and (- - -) $[Cu(L)_2Br_2]$–L_{ns} complexe.

The thermogravimetrical decomposition curves for the complexes are presented in Fig. 1. The initial decomposition of the labile solids begins at ambient temperature and is complete with the formation of $CuCl_2$ and $CuBr_2$ at 570 K. In each case, a stable intermediate of composition $Cu(L)_2X_2$ is formed. The TG–DTG curves do not show it clearly, but the DSC curves (Fig. 2) refer to a complex endothermic decomposition process.

A suggested first step in the decomposition of the parent compounds is made by taking into account the composition of the intermediates, $Cu(L)_2X_2$, and copper(II) halides, CuX_2, as final product. It was observed that the chloro complex lost 1.67 mol of ligand and the bromide complex 1.76 mol of ligand as follows:
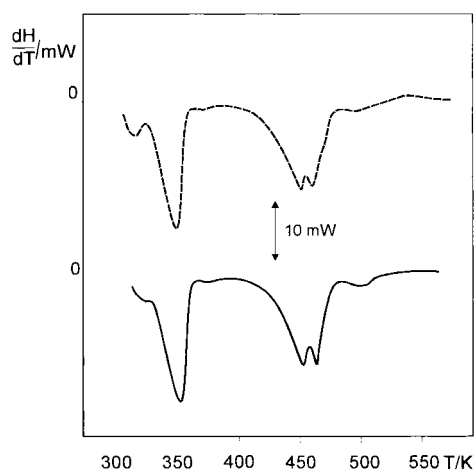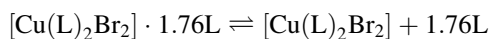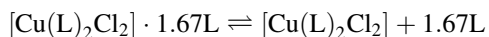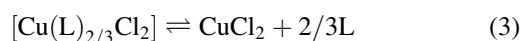
$$[Cu(L)_2Cl_2] \cdot 1.67L \rightleftharpoons [Cu(L)_2Cl_2] + 1.67L$$

$$[Cu(L)_2Br_2] \cdot 1.76L \rightleftharpoons [Cu(L)_2Br_2] + 1.76L$$

Fig. 2. DSC curves of (———) $[Cu(L)_2Cl_2]$–L_n and (- - -) $[Cu(L)_2Br_2]$–L_n.

The formation of the chloro intermediate, $Cu(L)_2Cl_2$, is complete at a somewhat lower temperature (350 K) than that of the bromo intermediate, $Cu(L)_2Br_2$, (370 K). The further decomposition of the intermediates begins at almost the same temperature (>420 K) in both cases. The course of the decomposition of the intermediates is also a complex one. From the TG data, the following decomposition scheme is suggested for the chloride complex:

$$[Cu(L)_2Cl_2] \rightleftharpoons [Cu(L)Cl_2] + L \qquad (1)$$

$$[Cu(L)Cl_2] \rightleftharpoons [Cu(L)_{2/3}Cl_2] + 1/3L \qquad (2)$$

$$[Cu(L)_{2/3}Cl_2] \rightleftharpoons CuCl_2 + 2/3L \qquad (3)$$
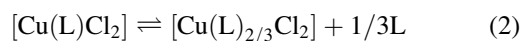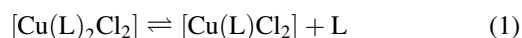
In the TG curve for the bromide complex, steps (1) and (2) are not well separated. However, the DSC curves (Fig. 2) also show a similar decomposition mechanism for the bromide complex.

These observations are consistent with the room-temperature X-ray data for the parent compounds and intermediates, Table 4, which are very similar, indicating a zeolitic or host–guest interaction. The mechanism is valid over the composition range from four-to-two ligand molecules. These loosely bonded molecules do not take part in the true co-ordination and are probably placed in infinite tunnels. This is also confirmed by the similarity in the electronic absorption bands. The host–guest interaction is reversible: at temperatures >350 K, the stable compound is

Table 4
XRD data of the complexes

	$[Cu(L)_{4\leftrightarrow2}Cl_2]$	$[Cu(L)_{4\leftrightarrow2}Br_2]$
	12.00	11.97
a/Å	13.92	14.09
	3.937	4.183
β/^{0}	91.71	93.10
V/Å^3	657.0	704.5
Z	2	2
D_{calc} (4 ligs.)/(g cm^{-3})	2.56	2.80
D_{calc} (2 ligs.)/(g cm^{-3})	1.66	1.92

$Cu(L)_2X_2$, while at ambient temperature in saturated ligand vapour, the formation of $[Cu(L)_2X_2]\cdot L_n$ complex ($n\leq2$) occurs.

4. Conclusion

Since the samples have a zeolite structure, they should be regarded as having stoichiometries $[Cu(L)_2Cl_2]$ or $[Cu(L)_2Br_2]$ with a variable increased composition up to two extra non-coordinated ligands. Confirmation was obtained from the X-ray measurements as well as from the electronic spectra, which indicated similar absorption bands for the complexes and their intermediates.

Acknowledgements

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