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PYRIDINE-TYPE COMPLEXES OF TRANSITION-METAL HALIDES XIV
Part III. Complexes with 2,4-, 2,6-, 3,4- and 3,5-lutidines

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Abstract

Compounds obtained by a solid–gas phase reactions between copper(II) chloride and bromide and 2,4-, 2,6- 3,4- and 3,5-lutidines were studied using thermogravimetry, far-infrared, electronic spectroscopy and X-ray diffraction. The results were compared with the corresponding data for the similar compounds with methylpyridines and 2,4,6-collidine. A special attention was paid to the host-guest phenomenon, a new structural feature of transition-metal halide complexes.

Keywords: copper(II) halide–lutidine (dimethylpyridine) complexes, host-guest phenomenon

Introduction

In our previous publications [1, 2] we studied copper(II) halide complexes with methylpyridines. This paper deals with 2,4-, 2,6- 3,4- and 3,5-lutidine (2,4-L, 2,6-L, 3,4-L and 3,5-L, respectively) complexes of copper(II) chloride and bromide. The aim of the study was to find the relationship between the methyl group(s) position and the newly observed host-guest phenomenon in copper(II) halide–methylpyridine complexes using spectroscopic and X-ray diffraction data of the originally obtained compounds and the intermediates which were formed during the thermal decomposition of the complexes.

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Experimental

The preparation of the compounds, the methods for analysis and the instrumentation are described in detail in our previous paper [1].

Results and discussion

The compounds were synthesised by a solid–gas phase reaction between the appropriate copper(II) halide and lutidine. As the atmosphere above the copper(II) salt was always saturated with the vapour of the given lutidine, always a compound with the highest co-ordination number was obtained instead of the most stable one. This means that the composition of some compounds has changed with time. The elemental analyses data of the freshly prepared samples and the intermediates are given in Table 1. It is apparent that the number of the ligands with a 2- or 6-methyl substituents, near to the co-ordinating nitrogen atom, is only two with both halide salts referring to a steric hindrance during the complex formation. With methyl substituents in position 3,4- and 3,5-, complexes with higher co-ordination number are forming. With 3,4-dimethylpyridine tetrakis(ligand) complexes were obtained with both of the copper(II) halides. With 3,5-dimethylpyridine and CuCl$_2$ the number of the ligands of the freshly prepared compound was somewhat more than 3, while with CuBr$_2$ this ligand gave a tris(ligand) complex.

Table 1 Elemental analysis data for the starting compounds and the intermediate (The intermediates are marked with*)

Compound	%C		%H		%N	
	calc.	found	calc.	found	calc.	found
Cu(2,4-L)$_2$Cl$_2$	48.21	47.63	5.20	5.00	8.03	7.93
Cu(2,6-L)$_2$Cl$_2$	48.21	48.23	5.20	5.17	8.03	8.04
Cu(3,4-L)$_4$Cl$_2$	59.72	60.03	6.44	6.50	9.95	10.04
*Cu(3,4-L)$_2$Cl$_2$	48.21	48.04	5.02	5.24	8.03	7.94
*Cu(3,5-L)$_2$Cl$_2$	48.21	48.01	5.20	5.17	8.03	7.82
Cu(2,4-L)$_2$Br$_2$	38.42	38.54	4.15	3.94	6.40	6.49
Cu(2,6-L)$_2$Br$_2$	38.42	38.03	4.15	3.92	6.40	6.32
Cu(3,4-L)$_4$Br$_2$	51.58	51.50	5.57	5.57	8.60	8.55
Cu(3,5-L)$_3$Br$_2$	46.29	45.19	5.00	4.76	7.71	7.52
*Cu(3,5-L)$_{1.5}$Br$_2$	32.83	34.97	3.54	3.62	5.47	5.80

All stable compounds contain two ligands except the tris(3,5-methylpyridine) copper(II) bromide complex which is stable in a temperature range up to 350 K where it decomposes to a compound with a composition of Cu(3,5-L)$_{1.5}$Br$_2$. The degradation of the intermediate starts almost immediately. The decomposition of the other stable complexes takes place in a temperature range of 400–450 K. The decomposition of the $Cu(3,5\text{-}L)_2Cl_{3.25}$ begins almost at room temperature, so the composition of the freshly prepared sample is not presented in Table 1 and was determined on the basis of the thermal decomposition curve according to the composition of the stable compound. In case of $Cu(3,4\text{-}L)_4Cl_2$, $Cu(3,5\text{-}L)_2Cl_{3.25}$ and $Cu(3,5\text{-}L)_3Br_2$ complexes, intermediates could be isolated and the composition of the obtained compounds was determined by elemental analysis. The results show that the composition of the intermediates corresponds to the complexes with two ligand molecules except in the case of $Cu(3,5\text{-}L)_3Br_2$ where the composition of the intermediate agree with $Cu(3,5\text{-}L)_{1.5}Br_2$. The thermal stability of this compound and the $Cu(3,4\text{-}L)_2Cl_2$ intermediate is poor and they were isolated by isothermal heating at the beginning of the decomposition of the parent compound (around 350 K in both cases).

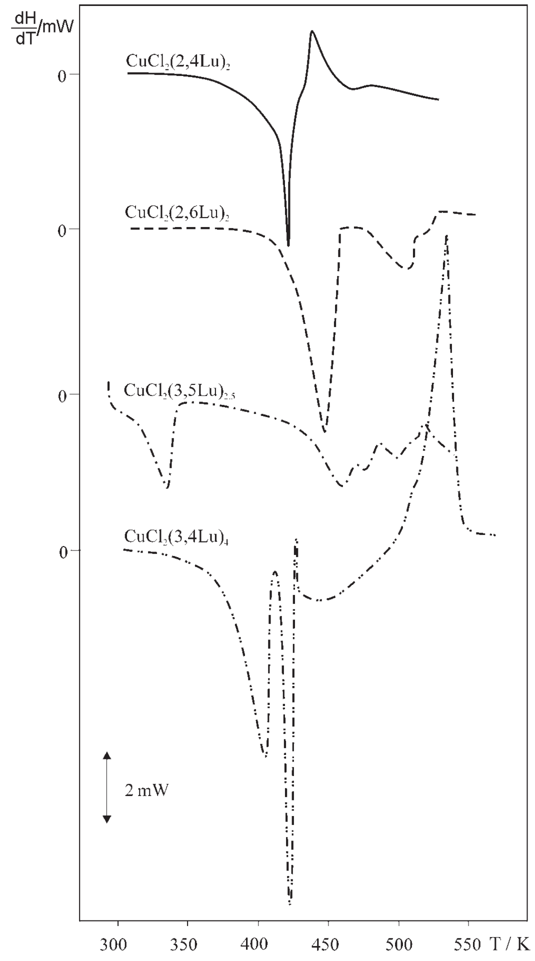

Fig. 1 DSC curves for the copper(II) chloride complexes with lutidines

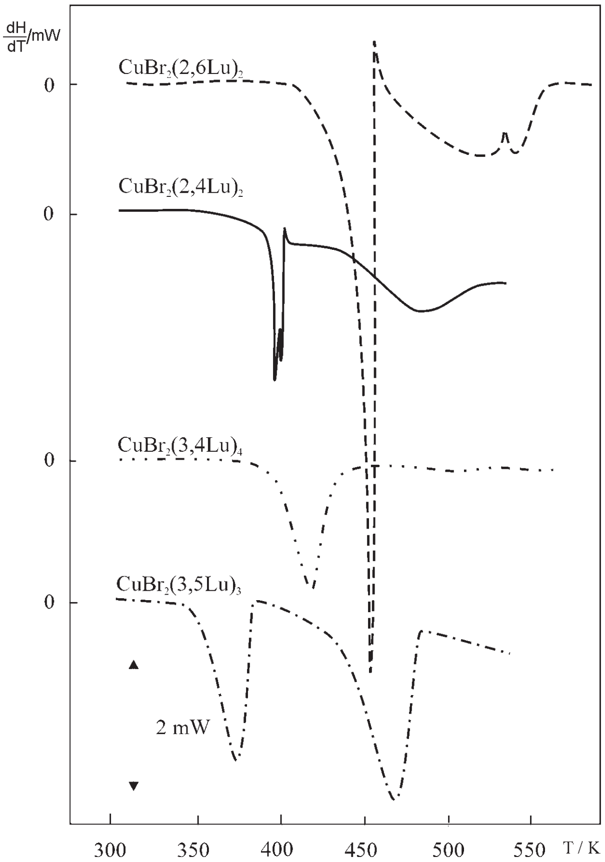

Fig. 2 DSC curves for the copper(II) bromide complexes with lutidines

The thermal decomposition curves of the compounds are presented in Figs 1–4. DSC curves (Figs 1 and 2) refer to different decomposition courses: the decomposition of $Cu(3,5\text{-}L)_3Br_2$, $Cu(3,4\text{-}L)_4Br_2$, $Cu(3,4\text{-}L)_4Cl_2$ and $Cu(2,6\text{-}L)_2Cl_2$ is endothermic up to 550 K. In case of other compounds during the decomposition an exothermic effect was observed which is very explicit at the decomposition of the $Cu(3,4\text{-}L)_4Cl_2$, referring probably to a structural rearrangement. In bromide complexes melting was observed in the first decomposition step, while there is no melting in case of chloride complexes.

The corresponding TG curves are presented in Figs 3 and 4 (DTG curves are omitted for the sake of a better introspection). The decomposition of $Cu(3,5\text{-}L)_2Cl_{3.25}$, calculated on the basis of the mass loss data can be presented by the following scheme,

$$Cu(3,5\text{-}L)_2Cl_{3.25} \rightarrow Cu(3,5\text{-}L)_2Cl_2 + 1.5\ (3,5\text{-}L)$$

$$Cu(3,5\text{-}L)_2Cl_2 \rightarrow Cu(3,5\text{-}L)Cl_2 + (3,5\text{-}L)$$

$$\mathrm{Cu(3,5\text{-}L)Cl_2 \rightarrow Cu(3,5\text{-}L)_{1/3}Cl_2{+}2/3\ (3,5\text{-}L)}$$

$$\mathrm{Cu(3,5\text{-}L)_{1/3}Cl_2 \rightarrow CuCl_2{+}1/3\ (3,5\text{-}L),}$$

while the decomposition of $Cu(3,5\text{-}L)_3Br_2$ takes place in two step to $CuBr_2$

$$\mathrm{Cu(3,5\text{-}L)_3Br_2 \rightarrow Cu(3,5\text{-}L)_{1.5}Br_2{+}1.5\ (3,5\text{-}L)}$$

$$\mathrm{Cu(3,5\text{-}L)_{1.5}Br_2 \rightarrow CuBr_2{+}1.5\ (3,5\text{-}L).}$$

The expected end product of the decomposition should be the corresponding copper(II) halide [1, 2] (or at higher temperatures CuO in curves recorded in an air atmosphere) in all the complexes. However, this is the case only with the compounds of $Cu(3,5\text{-}L)_3Cl_{3.25}$ and $Cu(3,5\text{-}L)_3Br_2$. Even the stability of these halides is poor. The de-

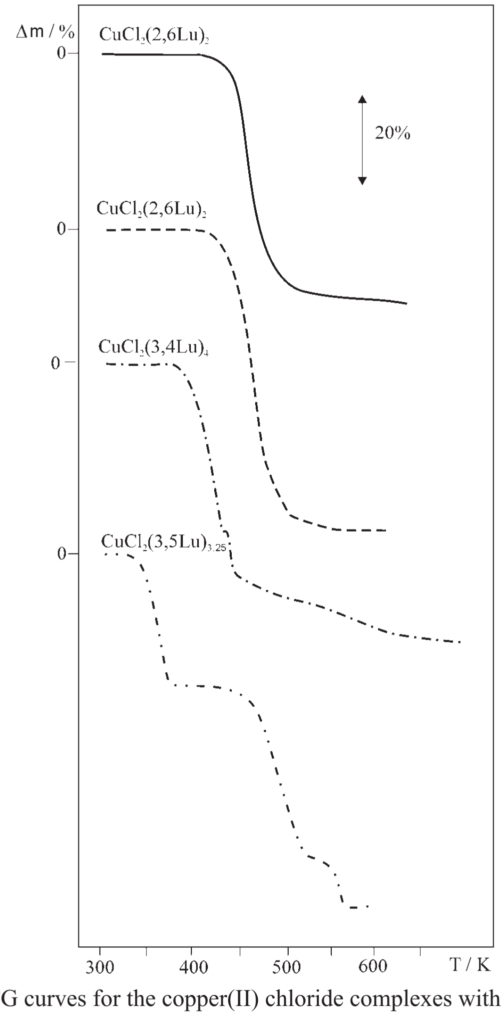

Fig. 3 TG curves for the copper(II) chloride complexes with lutidines

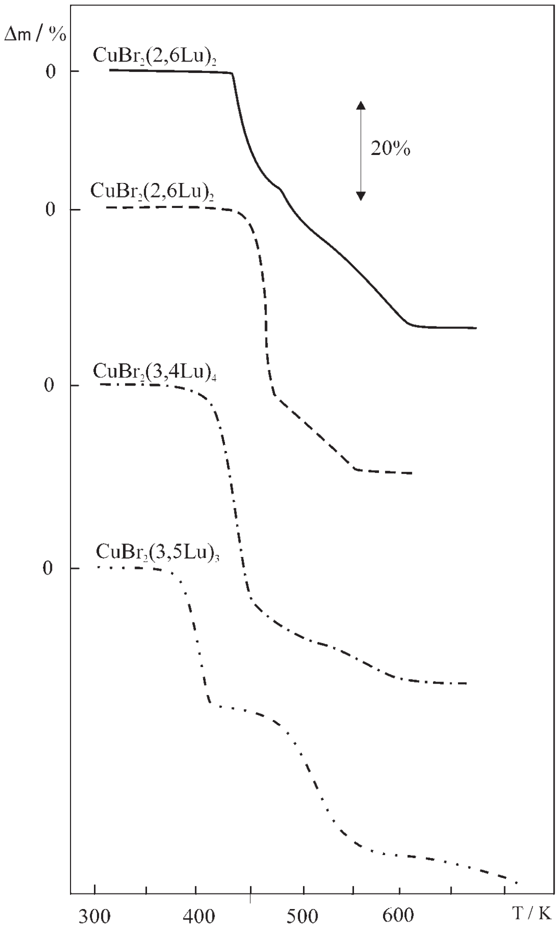

Fig. 4 TG curves for the copper(II) bromide complexes with lutidines

composition of the other compounds is continuous with a CuO end product around 800 K, except of the chloride complex with 3,4-lutidine where almost no residue is left. The chloride complex with 2,6-lutidine decomposes to CuCl (even in air), which is stable in a temperature range of about 50 K.

The FTIR spectra of the samples refer to a different geometry of the complexes [3]. Both the chloride and the bromide derivatives of 2,4-lutidine show a square planar arrangement [3–5]. In case of 2,6-lutidine analogues the bromide complex show a distorted octahedral, while the chloride one shows up as having a tetrahedral symmetry. For the chloride complex with 3,5-lutidine, the spectrum of the parent compound refers to an octahedral structure. Besides, bands of the free ligand were also observed [6] (531 sh, 284 sh, 209 w) indicating a host-guest interaction with the stable bis(ligand) compound which is forming during the thermal decomposition. According to the FTIR data, with losing the excess ligand the geometry of the parent compound changes to a square planar structure [3, 5]. The corresponding bromide intermediate appears to have a distorted octahedral symmetry. In the spectrum of the parent chloride complex with 3,4-lutidine [3, 5], the bands belonging to the ligand were splitted showing the presence of the free ligand ([6], 532 m, 421 sh, 257 s with participation of ν(CuN)) and the molecule shows an octahedral arrangement. The chloride intermediate spectrum indicates a tetrahedral, while the bromide analogue a distorted octahedral symmetry. The assignation of CuX, CuN stretchings and that of the ligand bands is given in Table 2.

Table 2 The assignation of the FTIR vibration bands

Compound	ν(CuX)	ν(CuN)	Ligand bands
$Cu(2,4\text{-}L)_2Cl_2$	317 vvs	252 s	543 m, 447 vs, 432 w, 298 s, 212 w
$Cu(2,6\text{-}L)_2Cl_2$	313 vvs, 296 vvs	240 vs	542 vw, 447 m, 284 m, 202 w
$Cu(2,4\text{-}L)_2Br_2$	242 vs	253 sh	543 m, 446 vs, 432 w, 298 m, 208 w
$Cu(2,6\text{-}L)_2Br_2$	229 vs	245 s	541 w, 448 m, 287 vs, 203 w
$Cu(3,4\text{-}L)_2Cl_2$	295 vvs, 286 vvs	257 s	358 m, 428 s, 191 vs, 164 m
$Cu(3,5\text{-}L)_2Cl_2$	294 vvs	249 s	542 w, 482 vw, 422 vw, 292 m, 224 w, 181 vs
$Cu(3,4\text{-}L)_2Br_2$	220 m	243 vs	542 vs, 433 vs, 187 vw
$Cu(3,5\text{-}L)_2Br_2$	217 m	241 vs	540 wm, 422 w, 292 m, 209 m

The electronic spectral data for the parent compounds and the intermediates are presented in Table 3 together with the type of the d→d transition. The geometry of the compounds determined on this basis is in accordance with the geometry suggested on the basis of the FTIR data.

Table 3 Electronic spectral data of the compounds

Compound	Peak position cm^{-1}	d → d transition	Geometry
$Cu(2,4\text{-}L)_2Cl_2$	17.391	$^2B_{1g} \rightarrow {}^2A_{2g}$	square planar
$Cu(2,4\text{-}L)_2Br_2$	16.474	$^2B_{1g} \rightarrow {}^2A_{2g}$	square planar
$Cu(2,6\text{-}L)_2Cl_2$	14.705	$^2T_2 \rightarrow {}^2E$	tetrahedral
$Cu(2,6\text{-}L)_2Br_2$	16.000	$^2E_g \rightarrow {}^2T_{2g}$	distorted octahedral
$Cu(3,4\text{-}L)_4Cl_2$	16.000	$^2E_g \rightarrow {}^2T_{2g}$	octahedral
$^*Cu(3,4\text{-}L)_2Cl_2$	14.706	$^2T_2 \rightarrow {}^2E$	tetrahedral
$Cu(3,4\text{-}L)_4Br_2$	16.520	$^2E_g \rightarrow {}^2T_{2g}$	distorted octahedral
$Cu(3,5\text{-}L)_4Cl_2$	14.598	$^2E_g \rightarrow {}^2T_{2g}$	octahedral
$^*Cu(3,5\text{-}L)_2Cl_2$	14.598	$^2B_{1g} \rightarrow {}^2A_{2g}$	square planar
$Cu(3,5\text{-}L)_3Br_2$	15.552	$^2E_g \rightarrow {}^2T_{2g}$	distorted octahedral

Table 4 The calculated and refined unit cell dimensions of the chloride and bromide complexes with 2,4- and 2,6-lutidine

Compound	Symmetry	Z	Unit cell parameters							Density	
			a/	b/	c/	α/	β/	γ/	V/	$D_{obs.}$	D_{calc}
				Å^3			deg		Å^3	g cm^{-3}	
$Cu(2,4\text{-}L)_2Cl_2$	monocl.	2	11.08	14.81	5.31	90.00	114.58	90.00	792.4	1.472	1.46
$Cu(2,4\text{-}L)_2Br_2$	tric.	1	11.34	14.75	5.50	90.00	114.50	90.00	835.6	1.756	1.73
$Cu(2,6\text{-}L)_2Cl_2$	monocl.	2	8.05	7.65	8.03	93.81	62.93	66.55	385.6	1.534	1.50
$Cu(2,6\text{-}L)_2Br_2$	tric.	1	8.01	8.44	7.85	63.94	67.14	57.85	394.2	1.865	1.84

Table 5 The calculated and refined unit cell dimensions of the chloride and bromide complexes with 3,4- and 3,5-lutidine

Compound	Symmetry	Z	Unit cell parameters							Density	
			a/	b/	c/	α/	β/	γ/	V/	$D_{obs.}$	D_{calc}
				Å^3			deg		Å^3	g cm^{-3}	
$Cu(3,4\text{-}L)_4Cl_2$	orto	4	9.79	14.80	9.78	90.00	90.00	90.00	1409.2		1.32_6
$Cu(3,4\text{-}L)_2Cl_2$	tetr.	8	14.64	14.64	12.54	90.00	90.00	90.00	2688.0		1.72_2
$Cu(3,4\text{-}L)_4Br_2$	orto	4	9.96	14.79	9.96	90.00	90.00	90.00	1458.7		1.48_3
$Cu(3,5\text{-}L)_2Cl_2$	monocl.	2	13.66	14.14	3.94	90.00	93.36	90.00	760.9	1.57	1.52
$Cu(3,5\text{-}L)_2Br_2$	monocl.	2	13.89	14.43	4.09	90.00	93.49	90.00	818.9		1.78

X-ray diffraction data on the bis(ligand) copper(II) halide compounds with 2,4- and 2,6-lutidines (the observed and the calculated densities within reasonable accuracy) correspond well to the given compositions. The index calculation of young samples is rather poor. Maximum one (normally 0) observed peak is not indexed. However, after storing several weeks or months at room temperature new sets of diffraction peaks are registered. The true history of this ageing is not yet understood. The observed and the calculated density data for these complexes are given in Table 4.

As the decompositions of 3,5-lutidine complexes starts almost at room temperature, the phase analysis of the stable compounds was performed. X-ray diffraction data of these stable intermediates show very large similarities, which is also reflected after indexing and refinements. According to TG-data the structure of 3,5-lutidine complexes seems to swallow at least three ligands. The quality of the diffraction characters of these two room temperature complexes is rather poor. The number of the measurable signals, apart from sets of the high-temperature type ones is low, which makes a throughout study worthless. Concerning the high-temperature composition, the number of ligands seems to correspond to two before a complete breakdown into solid halides. The amount of $CuBr_2$ complex was too small to make a true density measurement. $Cu(3,5\text{-}L)_2Cl_2$ complex has an observed density of 1.56 g cm^{-3}. With two ligands the density, calculated from X-ray data is 1.52 g cm^{-3}. The calculated and refined unit cell dimensions of the compounds are given in Table 5. The same data for the parent and the intermediate $CuCl_2$ complex with 3,4-lutidine and the $CuBr_2$ compound with the same ligand are presented in the same Table. The refined and indexed monophase X-ray patterns can be obtained upon request from the corresponding author or found in the near future in the JCPDS database.

Conclusions

Most of the copper(II) chloride and bromide complexes with mono- and dimethyl-substituated pyridines have a zeolite structure and 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, [1, 2]. In case of parent compounds the X-ray measurements as well as FTIR spectra beside the co-ordinated ligand molecules indicate the presence of free, non-coordinated ligands.

The number of the excess ligand molecules depends on the position of the methylsubstituent(s). With ligands having 2-methylsubstituents no host-guest phenomenon was observed, while ligands with a methyl group in position 4 give compounds with the highest co-ordination number. This is in accordance with the extent of the steric repulsion between the halides and the ring substituent(s).

From the comparison of the thermal decomposition curves it is evident that the corresponding bromido and chlorido complexes display a similar decomposition mechanism, suggesting that the chemical and structural properties of the complexes are dependent on the ligand structure rather than of the nature of the halide. In case of complexes with 4-methyl substituents the exothermic effect in DSC curves suggests a structural rearrangement during the decomposition. Besides, the very sharp endothermic maximum in bromide complexes refer to the melting of the compound. In case of chloride complexes no melting was observed.

2,4,6-collidine with copper(II) chloride gives a complex only with loosely bond ligand molecules, while with copper(II) bromide no complex formation takes place.

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