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PYRIDINE-TYPE COMPLEXES OF TRANSITION-METAL HALIDES
Part XV. Mn(II) chloride complexes with 3,4- and 3,5-lutidine

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Abstract

Manganese(II) chloride complexes with 3,4- and 3,5-lutidine have been prepared. The crystal symmetry and cell dimensions have been calculated on the basis of powder diffraction data. The compounds were characterised also by FT-IR spectrometry. The thermal decomposition of the complexes has been studied by thermogravimetry and DSC. By plotting densities *vs.* molar mass, the diagram obtained has correspondence to similar observations in other solid metal–lutidine complex systems.

Keywords: FT-IR spectrometry, host–guest phenomenon, manganese(II) chloride–lutidine (dimethylpyridine) complexes

Introduction

Pyridine and its derivatives are among the best-known heterocyclic nitrogen ligands. The co-ordination chemistry with pyridine-type ligands has been studied widely. Metal complexes of higher fatty acids with pyridine exhibit interesting thermochemical properties [1]. Transition metal salts with pyridine and methylpyridines often give inclusion compounds when stable guest molecules are placed in the holes, channels or layers of the host compound [2]. During the thermal treatment of such compounds, in the first decomposition step the guest molecules evaporate without destroying the host matrix.

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In our previous studies on copper(II) halide complexes [3–5] with methylpyridine derivatives, we have investigated the relationship between the methyl group(s) position and the structure as well as the thermal stability of the complexes formed. These compounds also reveal the host–guest phenomenon. The present paper deals with the structural characterisation and thermal decomposition of the manganese(II) chloride complexes with 3,4- and 3,5-lutidine. A special attention was paid to examine the 'zeolitic property' of the compounds.

Experimental

All chemicals used were of analytical reagent grade.

The compounds were synthesised by mixing warm methanolic solutions of the ligand (25 mmol) and manganese(II) chloride (2.5 mmol). The total volume of the mixture was about 5 cm^3. The very pale pink precipitates were obtained at room temperature. The compounds formed were washed with cold MeOH and Et_2O and dried at room temperature. Reaction time: 24 h.

The IR-spectra were recorded in the range of 4000–150 cm^{-1} on a Perkin Elmer System 2000 FT-IR spectrometer at room temperature using KBr pellets in the mid-IR range and polyethylene pellets in the far-IR range. The spectra were obtained with a resolution of 4 cm^{-1} and with a co-addition of 16 scans.

The thermal analysis in the temperature range up to 600 K was carried out in a flowing nitrogen atmosphere using a DuPont 2000 TA system with a thermobalance DuPont 951 TGA and a platinum crucible sample holder. The DSC curves were recorded in aluminium pan sample holder with an empty aluminium pan as reference. The heating rate was 10 K min^{-1}.

The unit cell parameters were obtained by transmission X-ray powder diffraction using a Guinier–Hägg focusing camera with Cu and $CrK_{\alpha1}$ radiation [3].

Results and discussion

The compounds were characterised by thermal methods, FT-IR spectrometry and X-ray powder diffraction.

Because of the steric hindrance of the methyl groups, with 3,5-lutidine (3,5-Lu) only bis(ligand) complex is obtained, while with 3,4-lutidine (3,4-Lu) a tetrakis derivative is formed. The thermogravimetric and DSC curves of the compounds are presented in Fig. 1. The decomposition is endothermic (DSC curves) in the full temperature range. The thermogravimetric curve shows that the bis(ligand) complex is stable up to 440 K. Its decomposition takes place in three steps which stoichiometry may be presented by the following scheme where in parenthesis the corresponding calculated value is given:

$Mn(3,5\text{-}Lu)_2Cl_2 \rightarrow Mn(3,5\text{-}Lu)Cl_2 + 3,5\text{-}Lu$ 33% (31.50%)

$Mn(3,5\text{-}Lu)Cl_2 \rightarrow Mn(3,5\text{-}Lu)_{0.5}Cl_2 + 0.5(3,5\text{-}Lu)$ 13% (15.75%)

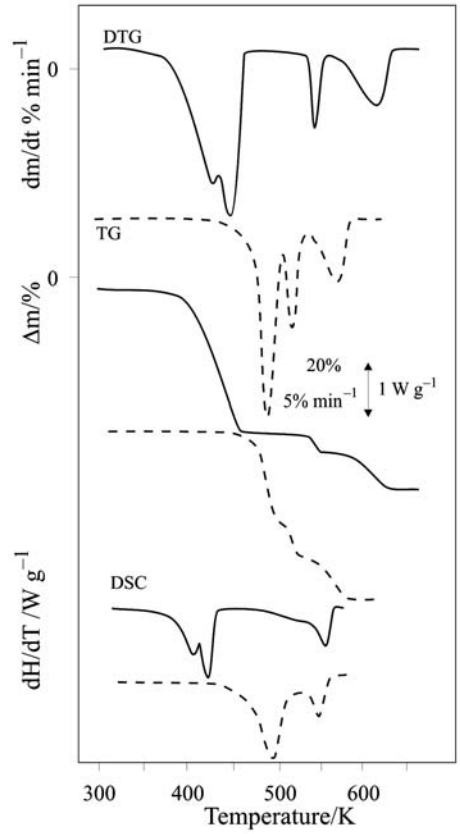

Fig. 1 DTG, TG and DSC curves of —— $Mn(3,4\text{-}Lu)_4Cl_2$ and ----- $Mn(3,5\text{-}Lu)_2Cl_2$

$Mn(3,5\text{-}Lu)_{0.5}Cl_2 \rightarrow MnCl_2 + 0.5(3,5\text{-}Lu)$ 15 % (15.75%)

The decomposition of $Mn(3,5\text{-}Lu)_2Cl_2$ is finished at 590 K.

The tetrakis(ligand) complex begins to decompose at room temperature and the composition of the thermally stable compound, calculated on the basis of the thermoanalytical data is $Mn(3,4\text{-}Lu)_{3.5}Cl_2$. Its decomposition begins at 380 K. In the temperature range of 380–450 K two superposed steps can be distinguished which refer to the evaporation of 1.5(3,4-Lu) and (3,4-Lu), respectively. The whole process can be presented as

$Mn(3,4\text{-}Lu)_{3.5}Cl_2 \rightarrow Mn(3,4\text{-}Lu)Cl_2 + 2.5(3,4\text{-}Lu)$ 54.3% (53.56%)

In the 450–530 K range no mass change is observed. The composition of the intermediate corresponds to $Mn(3,4\text{-}Lu)Cl_2$ which above 530 K decomposes in two steps to $MnCl_2$:

$Mn(3,4\text{-}Lu)Cl_2 \rightarrow Mn(3,4\text{-}Lu)_{2/3}Cl_2 + \frac{1}{3}3,4\text{-}Lu$ 7.1% (7.14%)

$Mn(3,4\text{-}Lu)_{2/3}Cl_2 \rightarrow MnCl_2 + \frac{2}{3}\,3,4\text{-}Lu$ 13.4% (14.28%)

The calculated values are given in parenthesis.

The intermediate has been isolated and its structure was examined by both the IR-spectrometry and transmission X-ray power diffraction.

The IR assignments for Mn(3,4-Lu)$_4$Cl$_2$ and its intermediate, Mn(3,4-Lu)Cl$_2$, are presented in Tables 1a and b, respectively, while those of Mn(3,5-Lu)$_2$Cl$_2$ are

Table 1a IR assignments of Mn(3,4-Lu)$_4$Cl$_2$

A	Assignment	A′	Assignment
3048 m	νCH	2948 m	νCH$_3$
2948 m	νCH$_3$	2948 m	νCH$_3$
2948 m	νCH$_3$	1465 sh	δ_eCH$_3$, δCH$_3$
2923 m	νCH$_3$	1066 sh	δ_eCH$_3$, δCH$_3$, γCCH$_3$
2923 m	νCH$_3$	1027 m	δ_eCH$_3$, δCH$_3$
1607 vs	νCC, νCN	825 s	γCCH, τCN
1560 m	νCN, νCC	719 sh	τCC, τCN, γCCH$_3$
1496 vs	βCCH, νCC, νCN	532 m	γCCH$_3$, τCC, τCN
1465 sh	δCH$_3$, νCCH$_3$	430 s	τCC, γCCH$_3$, γCCH, τCN
1447 s	δCH$_3$, δ_eCH$_3$, νCC	≈165 s	τCC, τCN
1419 s	δCH$_3$, δ_eCH$_3$	–	
1387 s	δ_eCH$_3$, δCH$_3$, βCCH	215 m	νMnCl
1377 m	βCCH, νCC, δ_eCH$_3$	195 m	νMnCl
1312 m	ring vibration	165 m	νMnN
1240 m	νCN, νCC, βCCH	–	
1199 vs	βCCH, βCCC, νCCH$_3$, δ_eCH$_3$	842 s	free ligand
1178 m	βCCH, νCC, νCCH$_3$	832 s	free ligand
1150 w	βCCH, νCC, νCCH$_3$	725 s	free ligand
1078 s	ring vibration	423 w	free ligand
1008 m	δ_eCH$_3$, δCH$_3$		
857 s	βCCC, βCNC, νCCH$_3$, βCCH		
755 m	βCCC νCCH$_3$		
607 s	βCCC, νCCH$_3$		
520 m	νCCH$_3$, βCCH$_3$		
413 w	βCCH$_3$		

listed in Table 2. The ligand's bands were assigned on the basis of the free ligand's spectrum [6], while the bands characteristic for the complex (νMnN and νMnCl) were determined using spectral data on Mn(*py*)$_2$Cl$_2$ (*py*=pyridin) [7]. In the IR spectrum of Mn(3,4-Lu)$_4$Cl$_2$ the shifts of the characteristic pyridine vibrations (605→612 and 423→430 cm^{-1}) are in accordance with the literature data. On the basis of the position of the νMnN vibration (180 cm^{-1}), for Mn(3,4-Lu)$_4$Cl$_2$ a polymeric octahedral geometry may be assumed. The presence of the free ligand bands in the spectrum of the freshly prepared sample refer to a host–guest interaction in the complex. On the basis of the IR-spectrum, to the structure of the isolated intermediate, Mn(3,4-Lu)Cl$_2$, also a polymeric octahedral structure may be ascribed.

Table 1b IR assignments of Mn(3,4-Lu)Cl$_2$

A	Assignment	A′	Assignment
2952 w	νCH$_3$	2952 w	νCH$_3$
2952 w	νCH$_3$	2952 w	νCH$_3$
2928 w	νCH$_3$	1458 sh	δ_eCH$_3$, δCH$_3$
2928 w	νCH$_3$	1458 sh	δ_eCH$_3$, δCH$_3$
1610 s	νCC, νCN	1059 w	δ_eCH$_3$, δCH$_3$, γCCH$_3$
1559 w	νCN, νCC	1017 m	δ_eCH$_3$, δCH$_3$
1502 m	βCCH, νCC, νCN	824 s	γCCH, τCN
1458 sh	δCH$_3$, νCCH$_3$	718 s	γCC, τCN, γCCH$_3$
1443 m	δCH$_3$, δ_eCH$_3$, νCC	529 m	γCCH$_3$, γCC, τCN
1420 m	δCH$_3$, δ_eCH$_3$	433 m	τCC, γCCH$_3$, γCCH, τCN
1390 m	δ_eCH$_3$, δCH$_3$, βCCH	–	
1377 m	βCCH, νCC, δ_eCH$_3$	235 br m	νMnCl
1313 w	ring vibration	205 br m	νMnCl
1242 w	νCN, νCC, βCCH	180 br m	νMnN
1202 s	CCH, CCC CCH$_3$ $_e$CH$_3$	–	
1177 w	CCH, CC CCH$_3$,	606 m	free ligand
1145 vw	CCH, CC, CCH$_3$	423 m	free ligand
1079 s	ring vibration		
1003 w	$_e$CH$_3$, CH$_3$		
917 w	$_e$CH$_3$		
859 s	βCCC, βCNC, νCCH$_3$, βCCH		
755 w	βCCC νCCH$_3$		
612 m	βCCC, νCCH$_3$		
521 m	νCCH$_3$, βCCH$_3$		
414 vw	βCCH$_3$		

Table 2 IR assignments for $\mathrm{Mn(3,5\text{-}Lu)_2Cl_2}$

	Assignment		Assignment
	A1		B2
3039 m	νCH	2950 m	$\nu\mathrm{CH_3}$
2950 m	$\nu\mathrm{CH_3}$	2916 m	$\nu\mathrm{CH_3}$
2916 m	$\mathrm{CH_3}$	1461 s	$\delta\mathrm{CH_3}$, $\delta_e\mathrm{CH_3}$, νCC
1601 s	νCC, νCN	1427 sh	$\delta\mathrm{CH_3}$
1461 s	βCCH, νCC, νCN, $\delta\mathrm{CH_3}$, $\delta_e\mathrm{CH_3}$	1376 m	βCCH, νCC, $\delta\mathrm{CH_3}$
1444 s	$\delta\mathrm{CH_3}$, $\delta_e\mathrm{CH_3}$	1331 m	βCCH, νCC, νCN
1376 m	βCCH, $\nu\mathrm{CH_3}$, νCN	1174 s	νCN, βCCH, νCC, $\nu\mathrm{CCH_3}$
1246 m	βCCH, βCCC, $\nu\mathrm{CCH_3}$, $\delta\mathrm{CH_3}$, $\delta_e\mathrm{CH_3}$	930 w	$\nu\mathrm{CCH_3}$, νCC, βCCH, βCCC
1148 s	ring vibration		B1
1037 s	νCC, νCN, βCCC	2950 m	$\nu\mathrm{CH_3}$
992 vw	$\delta_e\mathrm{CH_3}$, $\delta\mathrm{CH_3}$	1444 s	$\delta\mathrm{CH_3}$, $\delta_e\mathrm{CH_3}$
748 vs	βCCC, $\nu\mathrm{CCH_3}$, νCC, βCCH	1037 s	$\delta_e\mathrm{CH_3}$, $\delta\mathrm{CH_3}$
537 m	βCCC, $\nu\mathrm{CCH_3}$	930 w	γCCH
279 w	$\beta\mathrm{CCH_3}$	865 vs	ring vibration
	A2	698 vs	τCN, τCC
2950 m	νCH	412 w	$\gamma\mathrm{CCH_3}$, τCC, τCN
1444 s	$\delta\mathrm{CH_3}$, $\delta_e\mathrm{CH_3}$	–	
1037 s	$\delta_e\mathrm{CH_3}$, $\delta\mathrm{CH_3}$	2865 m	hybride band
959 w	ring vibration	2729 w	hybride band
943 w	γCCH	2493 w	hybride band
–		1861 w	hybride band
224 s	νMnCl	1795 w	hybride band
202 s	νMnCl		
170 s	νMnN		

In the spectrum of $\mathrm{Mn(3,5\text{-}Lu)_2Cl_2}$ both of the νMnCl bands (224 and 202 $\mathrm{cm^{-1}}$) and a νMnN band (170 $\mathrm{cm^{-1}}$) are assigned. The vibration at 397 $\mathrm{cm^{-1}}$ in the free 3,5-lutidine ligand is shifted to a higher frequency (412 $\mathrm{cm^{-1}}$). For this compound also a polymeric octahedral structure may be characteristic.

The calculated and refined unit cell dimensions for $\mathrm{Mn(3,5\text{-}Lu)_2Cl_2}$, $\mathrm{Mn(3,4\text{-}Lu)_4Cl_2}$ and those of the $\mathrm{Mn(3,4\text{-}Lu)Cl_2}$ intermediate are given in Table 3, while a part of characteristic X-ray patterns of the same compounds are presented in Tables 4a–c. Both of the 3,4-lutidine complexes are monoclinic, while the crystal structure of $\mathrm{Mn(3,5\text{-}Lu)_2Cl_2}$ is simple tetragonal. The full set of refined and indexed monophase

Table 3 The calculated and refined unit cell dimensions of the manganese(II) chloride complexes with 3,4-dimethylpiridine (3,4-Lu) and 3,5-dimethylpiridine (3,5-Lu)

Compound	Symmetry	Unit cell parameters		Z	V/Å^3	D_{calc}/g cm^{-3}
		a=9.793(7) Å	=90.00°			
Mn(3,4-Lu)$_4$Cl$_2$	monoclinic	b=15.424(9) Å	=100.3(2)°	2	1452	1.26
		c=9.769(9) Å	=90.00°			
		a=18.987(5) Å	=90.00°			
Mn(3,4-Lu)Cl$_2$	monoclinic	b=3.775(8) Å	=–101.0(6)°	4	879	1.62
		c=12.498(9) Å	=90.00°			
		a=14.125 Å	α=90.00°			
Mn(3,5-Lu)$_2$Cl$_2$	tetragonal	b=14.125 Å	=90.00°	2	760	1.49
		c=3.809 Å	=90.00°			

Table 4 The first part of characteristic X-ray powder pattern obtained by transmission Guinier-technique

h	*k*	*l*	2θ-obs.	2θ-calc.	*D*-obs.	Intensity
a) Mn(3,4-L)$_4$Cl$_2$						
1	0	0	9.183	9.171	9.6227	22
0	1	1	10.840	10.839	8.1551	98
0	2	0	11.470	11.464	7.7088	10
–1	0	1	11.801	11.775	7.4931	8
1	0	1	14.133	14.124	6.2614	51
0	2	1	17.717	17.716	6.0145	5
1	1	1	15.261	15.251	5.8011	5
–1	2	1	16.471	16.462	5.3776	13
1	3	0	19.555	19.554	4.5358	100
–1	1	2	19.933	19.948	4.4507	59
b) Mn(3,4-L)Cl$_2$ intermediate						
–1	0	1	7.840	7.825	44.2672	62
1	0	1	9.373	9.354	9.4283	100
0	0	2	14.446	14.430	6.1266	30
–2	0	2	15.691	15.687	5.6431	8
3	0	1	17.192	17.180	5.1537	17
2	0	2	19.761	18.770	4.7261	2
0	1	0	23.526	23.543	3.7786	11
1	1	0	24.045	24.028	3.6981	11
–1	1	2	27.669	27.652	3.1032	45
6	0	0	28.745	28.721	3.1032	6
c) Mn(3,5-L)$_2$Cl$_2$						
1	1	0	13.109	13.164	10.0297	100
2	1	0	20.856	20.884	6.3253	5
2	2	0	26.475	26.507	4.9997	17
3	1	0	29.683	29.703	4.4696	8
3	2	0	33.972	33.985	3.9190	6
0	0	1	34.974	34.987	3.8101	10
2	0	1	39.920	39.940	3.3539	5
2	1	1	41.090	41.098	3.2623	54
2	2	1	44.417	44.425	3.0289	6
3	1	1	46.539	46.537	2.8980	3

X-ray diffraction data can be obtained upon request from the corresponding author. Attempts to study the 3D-molecular arrangement in Mn(3,4-Lu)$_4$Cl$_2$ by single-crystal technique also confirmed the symmetry and dimensions derived by powder methods. However, the detailed structure was not of a quality to be published probably due to a complex twinning growth [8].

The corresponding copper(II) complexes show the host–guest interaction and the host molecules are those with two ligand molecules, i.e., by thermal decomposition of Cu(3,4-Lu)$_4$Cl$_2$ and Cu(3,5-Lu)$_{3.25}$Cl$_2$ bis(ligand) complexes are obtained [5]. On the contrary, in manganese(II) complexes the IR-spectra and the thermal properties may refer to the host–guest phenomenon only in the case of Mn(3,4-Lu)$_4$Cl$_2$. In the Mn(3,5-Lu)$_2$Cl$_2$ no zeolitic effect was observed. While the thermal stability of Cu(3,4-Lu)$_2$Cl$_2$ is poor, the corresponding Mn(3,4-Lu)$_2$Cl$_2$ cannot be isolated. In the case of the manganese(II) compound, the composition of the relatively stable intermediate is Mn(3,4-Lu)Cl$_2$. The thermal decomposition pattern of the corresponding manganese(II) and copper(II) complexes is also different. However, there is a good correlation between the density and the molar mass data of the corresponding manganese(II) and copper(II)–lutidine complexes as is shown in Fig. 2. We use this simple relation in order to enhance the veracity of the findings. The precision to obtain the proper cell dimension after having used a trial-and-error calculation with accurate data is very high. Of this reason, small deviations from the regular diagram forebode a structural property. On this basis it may be assumed a host and guest exchange in the case of Mn(3,4-Lu)$_4$Cl$_2$, as it is suggested by the presence of the free-ligand bands in the IR-sepctrum of the compound, and which have vanished in the spectrum of the corresponding intermediate.

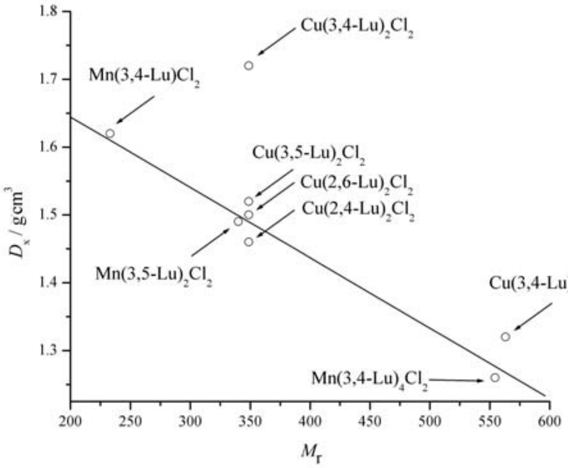

Fig. 2 Calculated density *vs*. molar volume and mass

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