ELSEVIER

Thermochimica Acta 340–341 (1999) 255–261

thermochimica acta

www.elsevier.com/locate/tca

Pyridine-type complexes of transition-metal halides XIII

Solid state studies of copper(II) chloride and bromide complexes with methylpyridines — Part II: complexes with 2- and 4-methylpyridine and 2,4,6-collidine

K. Mészáros Szécsényi[a,*], T. Wadsten[b], B. Carson[c], É. Bencze[d], G. Kenessey[e], G. Liptay[b]

[a]*Institute of Chemistry, Faculty of Sciences, University of Novi Sad, 21000 Novi Sad, Trg D. Obradovića 3, Yugoslavia*
[b]*Department of Inorganic Chemistry, Technical University of Budapest, H-1521, Budapest, Hungary*
[c]*Department of Applied Chemical and Physical Sciences, Napier University, Edinburgh, UK*
[d]*Institute of Isotopes and Surface Chemistry, Chemical Research Centre, Hungarian Academy of Sciences, PO Box 77, H-1525, Budapest, Hungary*
[e]*MERTCONTROL® Quality Control Co., PO Box 983, H-1245, Budapest, Hungary*

Accepted 6 August 1999

Abstract

This study is concerned with the reactions between copper(II) chloride and bromide with 2- and 4-methylpyridine and 2,4,6-collidine. The effects of the methyl groups(s)' position in a series of methylpyridines on the host–guest phenomenon in the formed copper(II) halide compounds were studied using thermogravimetry, far-infrared and electronic spectroscopy and X-ray diffraction. Copper(II) halide complexes with 4-methylpyridine and the copper(II) chlorido complex with 2,4,6-collidine exhibit zeolite properties. The reaction of copper(II) halides with 2-methylpyridine resulted in complex formation but no host–guest phenomenon was detected in these complexes. No complex formation was observed between 2,4,6-collidine and copper(II) bromide. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Copper(II) halide methylpyridine; 2,4,6-collidine complexes; Host–guest phenomenon

1. Introduction

In our previous paper [1] we reported a host–guest phenomenon in copper(II) halide — 3-methylpyridine complexes, a new structural feature among transition-metal halide complexes. In this work we have investigated the effect of the methyl group(s)' position on the structural characteristics and zeolite properties of a series of methylpyridines — copper(II) halide complexes using thermogravimetry, far-infrared and electronic spectroscopy and X-ray diffraction.

2. Experimental

The complexes were obtained by a solid–gas phase reaction and the intermediates were isolated as previously described in [1].

---

[*] Corresponding author. Fax: 381-21-55-662.

PII: S0040-6031(99)00270-1

The analyses were performed using the standard methods and instrumentation described in the same paper [1].

3. Results and discussion

3.1 Chemical characterisation of the parent compounds and intermediates included their elemental analysis (Table 1), recording of the electronic and far-infrared spectra and X-ray powder diffraction analysis (Tables 2–4). As in the case of the 3-methylpyridine complexes the composition of the parent 4-methylpyridine, (4-L), complexes changes with time, so the elemental analyses data in Table 1 are given only for the intermediates. The carbon, hydrogen and nitrogen content of the parent compounds, as well as TG data show that the number of the ligand molecules in these samples is close to four.

3.2 The 2-methylpyridine, (2-L), complexes are stable at room temperature. TG data agree with a composition of two ligand molecules in the compound, $[CuX_2(2\text{-}L)_2]$. In spite of the fact, that the complexes are stable at room temperature, the elemental analysis for the chlorido complex, performed several weeks later, gave a composition of $[CuCl_2(2\text{-}L)_{1.5}]$.

Table 1
Elemental analysis and electronic spectral data

Complex	C (%) (calculated)	H (%)	N (%) (found)	Peak position (cm^{-1})
$[CuCl_2(2\text{-}L)_{1.5}]$	39.23 (37.84)	3.86 (3.74)	7.66 (7.36)	17,699
$[CuCl_2(2\text{-}L)]$	31.66 (31.07)	3.10 (3.00)	6.15 (6.06)	19,801 (12,987)
$[CuBr_2(2\text{-}L)_2]$	35.18 (33.30)	3.44 (3.10)	6.84 (6.45)	18,692
$[CuCl_2(4\text{-}L)_2]$	44.94 (44.50)	4.44 (4.02)	8.73 (8.60)	14,814
$[CuBr_2(4\text{-}L)_2]$	35.18 (35.08)	3.44 (3.47)	6.84 (6.80)	14,389
$[CuCl_2(L)]$	37.59 (32.40)	4.33 (4.14)	5.48 (4.65)	9090

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

Compound	Symmetry	Unit cell parameters							Density D_{calc} (g cm^{-3})
		a (Å)	b (Å)	c (Å)	α(°)	β(°)	γ (Å^3)	V (Å^3)	
$[CuCl_2(2\text{-}L)_2]$	Triclinic	8.32	8.76	10.93	105.24	98.68	108.4	705.4	1.59
$[CuBr_2(2\text{-}L)_2]$	Triclinic	7.67	7.90	11.65	101.6	104.2	105.9	630.0	1.93
$[CuCl_2(4\text{-}L)_2]$	Monoclinic	17.58	3.949	9.573	–	98.6	–	657.0	1.62
$[CuBr_2(4\text{-}L)_2]$	Monoclinic	17.38	4.127	9.946	–	101.0	–	698.9	1.94

Table 3
The first part of characteristic X-ray powder pattern obtained by transmission Guinier-technique for $[CuCl_2(4\text{-}L)_4] \rightleftharpoons [CuCl_2(4\text{-}L)_2] + 2(4\text{-}L)$

h	k	l	2θ (observed)	2θ (calculated)	D (observed)	Interval
−1	0	1	9.943	9.942	8.889	100
2	0	0	10.169	10.170	8.691	53
1	0	1	11.283	11.284	7.836	14
−3	0	1	16.687	16.690	5.309	33
0	0	2	18.726	18.735	4.735	6
3	0	1	19.100	19.103	4.643	5
2	0	2	22.673	22.679	3.919	19
1	1	0	23.088	23.080	3.849	43
0	1	1	24.429	24.406	3.641	1

Table 4
The first part of characteristic X-ray powder pattern obtained by transmission Guinier-technique for $[CuBr_2(4\text{-}L)_4] \rightleftharpoons [CuBr_2(4\text{-}L)_2]+2(4\text{-}L)$

h	*k*	*l*	2*θ* (observed)	2*θ* (calculated)	*D* (observed)	Interval
−1	0	1	9.526	9.530	9.277	100
2	0	0	10.215	10.263	8.632	47
1	0	1	11.275	11.246	7.841	57
−3	0	1	16.342	16.342	5.420	8
0	0	2	18.199	18.195	4.871	19
−2	0	2	19.247	19.126	4.613	1
4	0	0	20.631	20.610	4.302	3
1	1	0	22.128	22.129	4.014	2
2	0	2	22.666	22.602	3.920	22
−1	1	1	23.715	23.575	3.749	9
2	1	0	23.972	23.888	3.709	3

3.3 The complex formation with 2,4,6-collidine (L) is less pronounced and it reacts only with copper(II) chloride. The amount of the ligand in the complex also changes with time. In a freshly prepared compound TG data suggest that the copper(II) ion is coordinated to more than one ligand.

3.4 The thermal decomposition curves for the complexes are presented in Figs. 1–4. The TG data are interpreted on the basis of the composition of the stable compounds. In the case of the 4-methylpyridine complexes the stable compounds are the intermediates and the corresponding copper(II) halides, and in the case of the 2-methylpyridine complexes the parent compounds and the corresponding copper(II) halides. For the chlorido copper(II) 2,4,6-collidine complex only the composition of the final product, $CuCl_2$, is reliable.

3.5 In Fig. 1 the thermogravimetric decomposition curves of 2- and 4 methylpyridine copper(II) chloride complexes are presented, whereas in Fig. 2 the decomposition of the corresponding bromido complexes is illustrated. Fig. 3 shows the TG and DTG curves of 2,4,6-collidine complex of copper(II) chloride and the decomposition of copper(II) bromide as no complex formation between the ligand and copper(II) bromide occurs.

3.6 Thermal decomposition of the 2-methylpyridine compounds begins at about 400 K for both the chlorido and bromido complexes (Figs. 1 and 2). In the case of the chlorido complex a stable intermediate formation occurs above 425 K with a formula of $[CuCl_2(2\text{-}L)]$. This compound is stable over 25 K range. Above 450 K a further decomposition takes place in two overlapping steps. The thermal decomposition of the chlorido complex is presented by the following

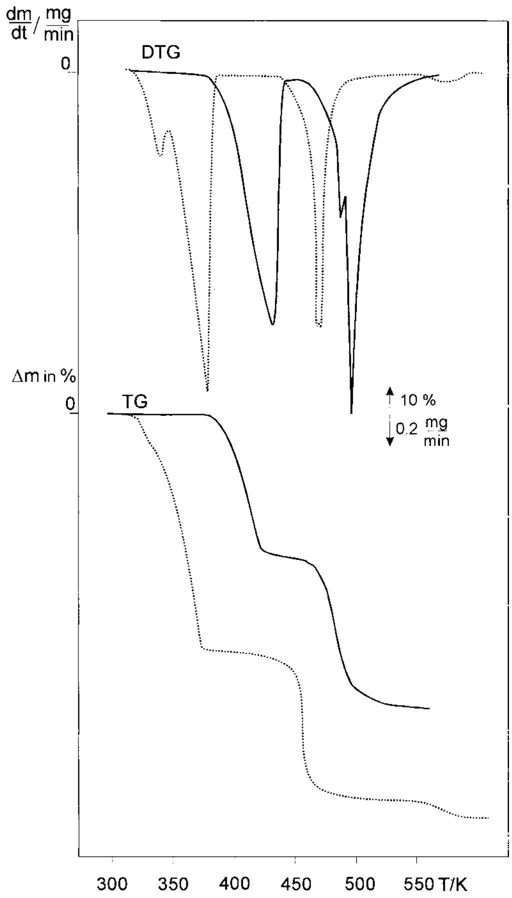

Fig. 1. TG and DTG curves of copper(II) chloride complexes with 2-methyl- (—) and 4 methylpyridine (······).

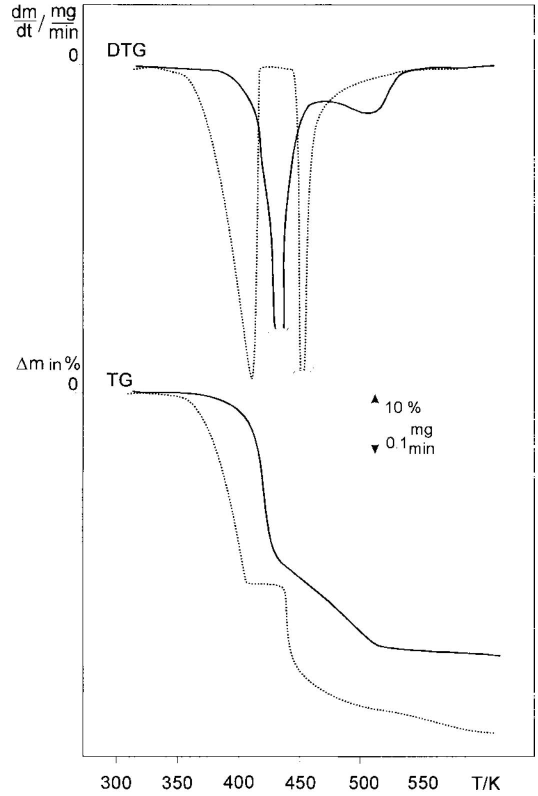

Fig. 2. TG and DTG curves of copper(II) chloride complexes with 2-methyl- (—) and 4 methylpyridine (······).

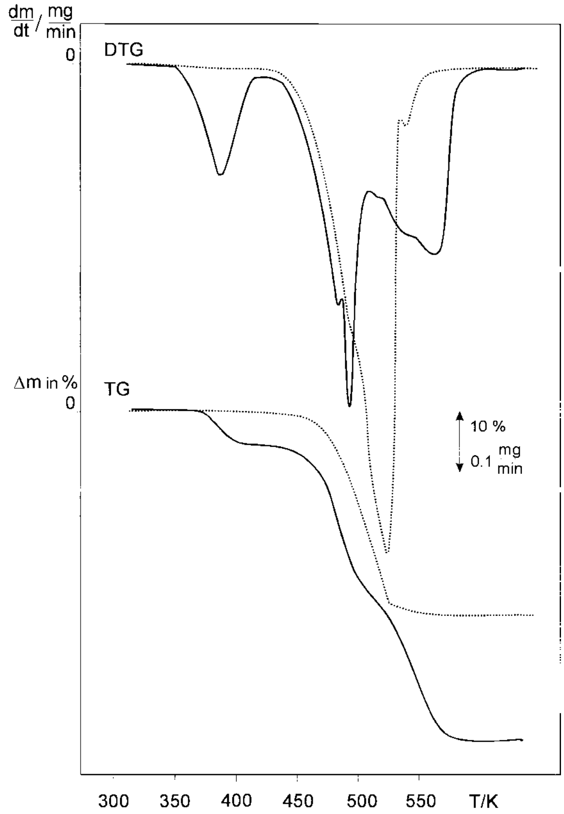

Fig. 3. TG and DTG curves of copper(II) 2,4,6-collidine complex (······) and copper(II) bromide.

scheme with the corresponding mass losses:

$[\mathrm{CuCl_2(2{-}L)_2}] \rightarrow [\mathrm{CuCl_2(2{-}L)}] + (2{-}L)$
27.5% (29.04%)

$[\mathrm{CuCl_2(2{-}L)}] \rightarrow [\mathrm{CuCl_2(2{-}L)_{0.5}}] + 0.5(2{-}L)$
15.0% (14.52%)

$[\mathrm{CuCl_2(2{-}L)_{0.5}}] \rightarrow [\mathrm{CuCl_2} + 0.5(2{-}L)$
15.0% (14.52%)

(The calculated values are given in parenthesis.)

3.7 The TG data for the parent chlorido compound give a composition with two ligands, while the data obtained by elemental analysis agree with a composition with less ligand in spite of the fact that the parent compound is stable at room temperature. The decomposition of the analogous bromido complex takes place in a similar way, but the corresponding steps are less separated.

3.8 The decomposition of the 4-methylpyridine complexes are also similar (Figs. 1 and 2) and the decomposition steps of the bromido complex are less separated. The decomposition of the bromido complex begins and ends at higher temperatures than that of the chlorido complex. The composition of the formed intermediates agrees with a formula of $[\mathrm{CuX_2(4\text{-}L)_2}]$. The course of the decomposition for the chlorido complex was interpreted on the basis of the composition of the intermediate and the copper(II) chloride as a final product:

$[\mathrm{CuCl_2(4{-}L)_{4.4}}] \rightarrow [\mathrm{CuCl_2(4{-}L)_4}] + 0.5(4{-}L)$
7.0% (7.06%)

$[\mathrm{CuCl_2(4{-}L)_4}] \rightarrow [\mathrm{CuCl_2(4{-}L)_2}] + 2(4{-}L)$
33.0% (35.32%)

$[\mathrm{CuCl_2(4{-}L)_2}] \rightarrow [\mathrm{CuCl_2(4{-}L)_{0.33}}] + 1.66(4{-}L)$
27.0% (29.31%)

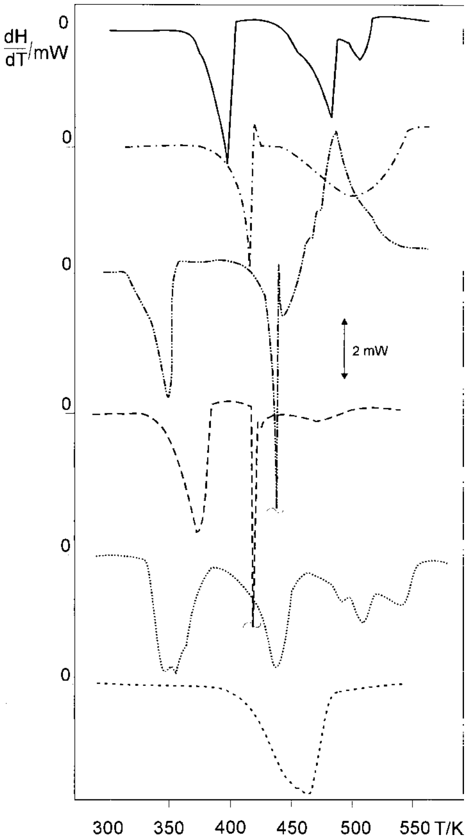

Fig. 4. DSC curves for the complexes: (—) $CuCl_2$ and (–·–·–·) $CuBr_2$ with 2-methylpyridine; (··–··–·) $CuCl_2$ and (– – –) $CuBr_2$ with 4-methylpyridine; (······) $CuCl_2$ with 2,4,6-collidine and (——) $CuBr_2$.

$$[CuCl_2(4\text{–}L)_{0.33}] \rightarrow CuCl_2 + 0.33(4\text{–}L)$$
6.5% (5.83%)

3.9 The thermal decomposition of the chlorido copper(II) — 2,4,6-collidine compound is a complex one. From TG data the following decomposition scheme may be suggested:

$$[CuCl_2(L)_{1.2}] \rightarrow [CuCl_2(L)] + 0.2L$$
6.0% (8.66%)

$$[CuCl_2(L)] \rightarrow [CuCl_2(L)_{0.5}] + 0.5L$$
21.0% (21.65%)

$$[CuCl_2(L)_{0.5}] \rightarrow CuCl_2 + 0.5L$$
27.0% (21.65%)

3.10 Stable intermediates are formed during the thermal decomposition of 2- and 4-methylpyridine chlorido copper(II) complexes and of 4-methylpyridine copper(II) bromide complex. For further analyses the intermediates were prepared by a freezing-out technique. Since the decomposition of the chlorido copper(II) 2,4,6-collidine complex in the temperature range from 380 to 420 K is very slow and the minimum of the DTG curve is close to zero, its intermediate was also isolated by the same technique. However, the composition of the intermediate did not agree with that obtained by the thermal analysis. For the composition of the intermediate TG data gave a formula of $[CuCl_2(L)]$, while by elemental analyses the composition of the compound agreed with $[CuCl_2(L)_{0.8}]$. The data obtained by elemental analysis and TG data for the intermediates of the 4-methylpyridine complexes were in accordance with composition of $[CuX_2(4\text{-}L)_2]$, where X stands for chloride or bromide. The composition of the chlorido copper(II) — 2-methylpyridine intermediate compound is consistent with the formula $[CuCl_2(2\text{-}L)]$. As copper(II) bromide is easily reducible, the bromido copper(II) compounds were heated up to 1000 K in an air atmosphere. The decomposition of the copper(II) bromide residue in all of the complexes began above 600 K. The end product of the decomposition around 900 K was, as expected, copper(II) oxide.

No reaction was observed between the copper(II) bromide and 2,4,6-collidine. The thermal decomposition curve corresponds to the reduction of the copper(II) bromide to copper(I) bromide at the same temperature (420 K) as in the case of the pure bromide salt even in air atmosphere.

3.11 In the FIR spectra of the parent 2-methylpyridine copper(II)-halide compounds, $[CuX_2(2\text{-}L)_2]$, the free 2-methylpyridine bands are not present [2]. The complexes have the same *cis*-square planar symmetry [the ν(Cu–N) and ν(Cu–X) bands of B_u symmetry cannot be separated]. In the case of the chlorido complex by thermal decomposition the symmetry of the parent compound is changed to a polymeric octahedral structure [3]: the $\nu(\text{Cu–Cl}) = 309\ cm^{-1}$ band of the parent compound in the spectrum of the intermediate is shifted to 196 and 181 cm^{-1}.

3.12 FIR spectra of the copper(II) halide 4-methylpyridine complexes for both the parent compounds and intermediates suggest an octahedral symmetry.

The characteristic bands are in accordance with literature data [4]: for the chlorido complexes ν(Cu–Cl) = 298 and 234 cm^{-1}, ν(Cu–N) = 260 cm^{-1}; for the bromido compounds ν(Cu–Br) = 236 and 200 cm^{-1}, ν(Cu–N) = 258 cm^{-1}. In the spectra of the parent compounds there are no free ligand bands. However, the increased intensity ratio of the ligand bands relative to the Cu–X bands in the parent compound compared with those of the intermediates may refer to a host–guest phenomenon in the 4-methyl pyridine complexes.

In the FIR spectrum of the parent chlorido copper(II) collidine complex the ν(Cu–Cl) and ν(Cu–N) bands at 309 and 267 cm^{-1}, respectively, suggest complex formation with a *cis*-square planar symmetry. The presence of the free collidine peaks [5] (518 cm^{-1}, s, 276 cm^{-1}, sh, 227 cm^{-1}, m, 187 cm^{-1}, s) in the spectrum refer to a host–guest phenomenon. In the intermediate, the bands of free collidine disappear and the complex symmetry changes, it becomes tetrahedral [ν(Cu–Cl) = 330 wm, 307 vs, and ν(Cu–N) = 245 m].

The electronic spectra (Table 1) suggest also different environments for the central atom in the 4-methyl and 2-methylpyridine complex. The $^2E_g \rightarrow {}^2T_{2g}$ transitions [6] observed in the UV/VIS spectra of the parent and intermediate 4-methylpyridine complexes are in accordance with an octahedral geometry suggested by the FIR-data analysis. The $^2B_{1g} \rightarrow {}^2A_{2g}$ transitions [7,8] in the UV/VIS spectra of the 2-methylpyridine complexes support the square-planar structure suggested by the FIR data. In the case of the chloro copper(II) — 2,4,6-collidine intermediate the tetrahedral geometry suggested by FIR data is supported also by the electronic spectrum of the compound [9].

The results of the X-ray studies of the compounds are also in agreement with the proposed compositions for the parent compounds and intermediates as well. The calculated and refined unit cell dimensions and the first part of the characteristic X-ray pattern for the 4-methylpyridine complexes are presented in Tables 2–4. The cell dimensions of the 2-methylpyridine compounds are given also in Table 2.

4. Conclusions

Fig. 4. shows the DSC curves for all of the samples. From the comparison of the curves it is evident that the corresponding bromido and chlorido complexes display a similar decomposition mechanism, which suggests that the chemical and structural properties of the complexes are dependent on the ligand structure rather than of the nature of the halide. However, the decomposition steps are better separated in the chlorido complexes. As is expected, the decomposition temperature of the compounds depends on the position of the methyl group(s) in the pyridine ring. The highest thermal stability of the intermediate for both the chlorido (over a 70 K range) and bromido (over a 50 K range) complexes is observed in the compounds with 4-methylpyridine. The same complexes also exhibit zeolitic effect. The last decomposition step of the 4-methylpyridine chlorido complex is accompanied by a strong exothermic effect suggesting structural rearrangement during the decomposition of the unstable $[\text{CuCl}_2(\text{4-L})_{0.33}]$ intermediate.

The very sharp endothermic maxima appearing in Fig. 4 around 400 K may refer also to the melting of the samples during the decomposition. The process of melting was examined by hot-stage microscopy (NU-2, Carl Zeiss, Jena). It was found that the bromido complexes melted during the decomposition, while no melting was observed in the case of the chlorido compounds.

The low starting decomposition temperature in the case of the 4-methylpyridine complexes and 2,4,6-collidine complex with copper(II) chloride refer to loosely bonded ligand molecules, which means that the composition of the parent compounds is not stable. In these compounds the FIR and X-ray diffraction data confirmed the presence of a host–guest phenomenon, while in the 2-methylpyridine complexes no zeolite properties were observed. Between 2,4,6-collidine and copper(II) bromide no complex formation was detected.

Acknowledgements

The authors would like to thank the Carnegie Trust for the Universities of Scotland for the support provided for this work. Part of the present contribution (T.W.) has been possible thanks to the exchange program between the Hungarian and the Royal Swedish Academy of Sciences and partly supported by the Hungarian OTKA Foundation (T-019555). The authors would also like to thank the Domus Hungarica Scientiarum Artiumque Foundation for their support.

References

[1] M. Szécsényi, T. Wadsten, B. Carson, É. Bencze, G. Kenessey, F.F. Gaál, G. Liptay, Thermochim. Acta, 316 (1998) 75.
[2] C.W. Frank, L.B. Rogers, Inorg. Chem. 5 (1966) 615.
[3] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1986.
[4] R.J.H. Clark, C.S. Williams, Inorg. Chem. 4 (1965) 350.
[5] J.A. Draeger, Spectrochim. Acta 39A (1983) 809.
[6] J.R. Allan, N.D. Baird, A.L. Kassyk, J. Therm. Anal. 16 (1979) 79.
[7] F.A. Cotton, J.J. Wise, Inorg. Chem. 6 (1967) 917.
[8] W.E. Hatfield, T.S. Piper, Inorg. Chem. 1 (1964) 970.
[9] C.N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, London, 1963.