SYNTHESIS, CRYSTAL STRUCTURE AND SPECTRAL PROPERTIES OF COPPER(II) AND COBALT(II) 3-METHYLTHIOPHENE-2-CARBOXYLATO COMPLEXES WITH FUROPYRIDINES

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Abstract: The synthesis and characterization of eleven new Cu(II) and Co(II) complexes is reported. The complexes were characterized by elemental analyses, infrared and electronic spectra. Copper(II) with 3-methylthiophene-2-carboxylic acid (HMTK) forms a dinuclear complex of the acetate type [$Cu_2(MTK)_4(H_2O)_2$]. By reaction of this complex with 2-metylfuro[3,2-*c*]pyridine (MeFP), not only acetate type complexes [$Cu_2(MTK)_4L_2$] (L= FP, MeFP) were obtained, but also monomeric complex [$Cu(MTK)_2(FP)_2$]. In the cases of [1]benzofuro[3,2-*c*]pyridine (BFP) and 2-(3-trifluoromethyl-phenyl)furo[3,2-*c*]pyridine (CF_3FP) only monomeric complexes [$Cu(MTK)_2L_2$] (L = BFP, CF_3FP) were obtained. It is possible to observe, that with increasing amount of the ligand, the yield of monomeric complexes increases too. In monomeric complexes, the carboxylic group of anionic MTK binds to atom Cu(II) by asymmetrically chelating *O,O*-coordination. The crystal structure of the complex [$Cu(MTK)_2(MeFP)_2$] was determined by X-ray single crystal structure analysis. The copper(II) atom lies in the crystallographic centre of symmetry in an distorted tetragonal-bipyramidal arrangement. The structure of this complex confirms an asymmetric chelate coordination of the carboxylic group. HMTK and Cobalt(II) form coordination compound [$Co(H_2O)_6$]$(MTK)_2$ with assumed ionic mode of coordination of anionic MTK. With furopyridines monomeric complexes [$Co(MTK)_2L_2$] (L= FP, MeFP, BFP, CF_3FP) with distorted octahedral coordination polyhedron around Co(II), were formed.

Key words: complex, copper(II), cobalt(II), furopyridine, carboxylate

1. Introduction

Derivatives of thiophene-2-carboxylic acid alone and their coordination compounds are interesting from biological as well as structural point of view (PANAGOULIS, *et al.*, 2007). The thiophene-2-carboxylic acid is an hypocalcemic agent and is effective in lowering the level of serum-glucose and fatty acids (RIBEIRO and SANTOS, 2008).

In this paper, we describe synthesis, spectral properties and crystal structure of 3-methylthiophnenecarboxylatecopper(II) and cobalt(II) complexes and their adducts with *N*-heterocyclic ligands: [$Cu_2(MTK)_4L_2$] (L=H_2O, FP, MeFP); [$Cu(MTK)_2L_2$] (L=FP, MeFP, BFP, CF_3FP); [$Co(H_2O)_6$]$(MTK)_2$, [$Co(MTK_2)L_2$] (L=FP, MeFP, BFP,

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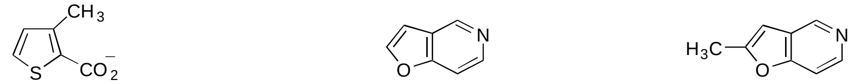
CF_3FP). The crystal and molecular structure of one of the complexes under study $[Cu(MTK)_2(MeFP)_2]$ has also been studied by X-ray structure analyses. Topological structures and abbreviations of heterocyclic ligands under study are given in Fig. 1.



3-methyltiophene-2-carboxylate
MTK

furo[3,2-c]pyridine
FP

2-metylfuro[3,2-c]pyridine
MeFP

2-(3-trifluoromethylphenyl)furo[3,2-c]pyridine
CF_3FP

[1]benzofuro[3,2-c]pyridine
BFP

Fig. 1. Structures and abbreviations of heterocyclic ligands.

2. Material and methods

2.1 Chemical reagents, analysis and physical measurements

All used chemicals were of reagent grade and used without further purifications. Derivatives of furopyridine (FP, MeFP, BFP and CF_3FP) have been prepared using Eloy-Derickere procedure (ELOY and DERYCKERE, 1971).

Cobalt and copper were determined by chelatometry after mineralization of the complexes. Carbon, hydrogen, nitrogen and sulfur were determined by microanalytical methods (Thermo Electron Flash EA 1112). Analytical data for the complexes are given in Table 1. Electronic spectra of the powdered samples were recorded on a Specord 200. IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer (Thermo Scientific).

2.2 Crystallography

Data collection for $[Cu(MTK)_2(MeFP)_2]$ (complex **4**) was obtained using Siemens P4 diffractometer (Siemens, XEMP. Version 4.2, 1990) with graphite monochromated MoK_{α} , radiation at 293 K. The diffraction intensities were corrected for Lorenz and polarization factors. The structures were solved by the heavy atom method with SHELXS-86 (G. M. SHELDRICK, 1985), subsequent Fourier synthesis using SHELXL-97 (G. M. SHELDRICK, 1997) and refined by the fullmatrix least-square method on all F^2 data using the program SHELXL-97 (G. M. SHELDRICK, 1997). Geometrical analysis was performed using SHELXL-97 [10]. Crystal data and conditions of data collection and refinement are reported in Table 2.

2.3 Preparation of the complexes

$[Cu_2(MTK)_4(H_2O)_2]$ (1): NaOH (0.6 g; 9 mmol) was dissolved in water (10 cm^3) and HMTK was added (1.28 g; 9 mmol). pH was adjusted to 7. Solution of $CuSO_4$ (1.12 g;

4.5 mmol) in water (5 cm^3) was then added. The mixture was stirred for 1 h and precipitate was filtered off. The precipitate was washed with water and dried at room temperature. Yield: 0.9 g.

Table 1. Cu(II) a Co(II) analytical data for the complexes.

Compounds	Empirical formula	Formula weight (g mol^{-1})	Calcd / Found (%)				
			M	C	H	N	S
$[Cu_2(MTK)_4(H_2O)_2]$	$C_{12}H_{12}CuO_5S_2$	363.9	17.46	39.61	3.32	-	17.62
1			17.98	39.65	3.23	-	17.78
$[Cu_2(MTK)_4(FP)_2]$	$C_{19}H_{15}CuNO_5S_2$	465.00	13.66	49.08	3.25	3.01	13.79
2			14.15	48.60	3.12	2.67	13.44
$[Cu_2(MTK)_4(MeFP)_2]$	$C_{20}H_{17}CuNO_5S_2$	479.03	13.26	50.15	3.57	2.92	13.39
3			13.74	49.87	3.48	2.70	13.24
$[Cu(MTK)_2(MeFP)_2]$	$C_{28}H_{24}CuN_2O_6S_2$	612.18	10.38	54.93	3.95	4.57	10.47
4			10.84	54.44	3.91	4.34	10.05
$[Cu(MTK)_2(BFP)_2]$	$C_{34}H_{24}CuN_2O_6S_2$	684.24	9.28	59.68	3.53	4.09	9.37
5			9.66	59.65	3.51	4.08	8.87
$[Cu(MTK)_2(CF_3FP)_2]$	$C_{40}H_{26}CuF_6N_2O_6S_2$	872.32	7.28	55.07	3.00	3.21	7.35
6			7.65	54.72	2.86	3.11	6.92
$[Co(H_2O)_6](MTK)_2$	$C_{12}H_{22}CoO_{10}S_2$	449.36	13.11	32.07	4.93	-	14.27
7			12.63	31.99	4.43	-	14.53
$[Co(MTK)_2(FP)_2]$	$C_{26}H_{20}CoN_2O_6S_2$	579.51	10.17	53.89	3.48	4.83	11.06
8			9.88	54.38	3.80	4.67	10.59
$[Co(MTK)_2(MeFP)_2]$	$C_{28}H_{24}CoN_2O_6S_2$	607.57	9.70	55.35	3.98	4.61	10.55
9			9.36	54.87	4.08	4.51	10.56
$[Co(MTK)_2(BFP)_2]$	$C_{34}H_{24}CoN_2O_6S_2$	679.63	8.67	60.09	3.56	4.12	9.43
10			8.50	60.58	3.70	4.46	8.84
$[Co(MTK)_2(CF_3FP)_2]$	$C_{40}H_{26}CoF_6N_2O_6S_2$	867.71	6.79	55.37	3.02	3.23	7.39
11			7.12	54.93	3.12	3.35	6.98

$[Cu_2(MTK)_4(FP)_2]$ (2); $[Cu_2(MTK)_4(MeFP)_2]$ (3); $[Cu(MTK)_2(MeFP)_2]$ (4): Complex **1** (0.382 mg; 0.525mmol) was dissolved in methanol (9 cm^3) and ligand (FP, MeFP; 5 mmol) in methanol (3 cm^3) was added. Solution was then heated to 50°C and stirred for 1 h. The precipitate formed during the reaction was filtered off, washed with methanol and dried at r. t. Blue filtrate evaporated at r. t. and crystals were formed and separated. Yield: complex **2** - 0.5 g; complex **3** - 0.4 g; complex **4** - 0.2 g.

$[Cu(MTK)_2(BFP)_2]$ (5); $[Cu(MTK)_2(CF_3FP)_2]$ (6): Complex **1** (0.382 mg; 0.525mmol) was dissolved in methanol (9 cm^3) and ligand (BFP, CF_3FP, 5 mmol) in methanol (9 cm^3) was added. Solution was then heated to 50°C and stirred for 1 h. The precipitate formed during the reaction was filtered off, washed with methanol and dried at r. t. Yield: complex **5** - 1.5 g; complex **6** - 0,7 g.

$[Co(H_2O)_6](MTK)_2$ (7): NaOH (0.14 g; 3.5 mmol) was dissolved in water (10 cm^3) and HMTK was added (0.5 g; 3.5 mmol). pH was adjust to 7. Solution of $CoSO_4$ (0.49 g; 1.75 mmol) in water (5 cm^3) was then added. Mixture then evaporated at r. t. and subsequent crystals were separated. Yield: 1.1 g.

$[Co(MTK)_2(FP)_2]$ (8); $[Co(MTK)_2(BFP)_2]$ (10); $[Co(MTK)_2(CF_3FP)_2]$ (11); The complex **7** (0.449 g; 1 mmol) was dissolved in methanol (5 cm^3) and ligand (FP, BFP, CF_3FP; 5 mmol) in methanol (3 cm^3) was added. Solution was then heated to 50°C and stirred for 1 h. Mixture then evaporated at r. t. and subsequent crystals were separated. Yield: complex **7** - 2.1 g; complex **10** - 2.1 g; complex **11** - 0.9 g.

$[Co(MTK)_2(MeFP)_2]$ (9): The complex **7** (0.449 g; 1 mmol) was dissolved in DMF (15 cm^3) and ligand (MeFP; 5 mmol) in DMF (5 cm^3) was added and stirred for 1 h. Mixture then evaporated at r. t. Yielded crystals were separated and dried at r. t. Yield: 0.4 g.

Table 2. Crystal data and structure refinement for $[Cu(MTK)_2(MeFP)_2]$ (complex **4**).

Identification code	mk75
Empirical formula	C28H24CuN2O6S2
Formula weight	612.19
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 6.352(1) Å α = 82.53(1)^O
	b = 10.489(1) Å β = 80.95(1)^O
	c = 10.501(1) Å γ = 87.09(1)^O
Volume	684.74(14) $Å^3$
Z, Calculated density	1, 1.485 Mg/m^3
Absorption coefficient	0.995 mm^{-1}
F(000)	315
Crystal size	0.12 x 0.4 x 0.5 mm
θ range for data collection	4.17 to 26.35^O.
Limiting indices	$-1<=h<=1$, $-13<=k<=13$, $-13<=l<=13$
Reflections collected / unique	1384 / 692 [R(int) = 0.0754]
Completeness to θ = 26.35	24.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	692 / 0 / 179
Goodness-of-fit on F^2	0.901
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0383, wR2 = 0.0886
R indices (all data)	R1 = 0.0491, wR2 = 0.0957
Extinction coefficient	0.000(5)
Largest diff. peak and hole	0.165 and -0.128 e. $Å^{-3}$

3. Results and discussion

3.1 Description of crystal structure of $[Cu(MTK)_2(MeFP)_2]$

The structure of $[Cu(MTK)_2(MeFP)_2]$ (complex **4**) is shown in Fig. 2. The copper(II) atom is bonded in *trans* square-planar arrangement to two nitrogen atoms of two methylfuropyridine molecules [Cu – N1 = 2.050 Å] and one carboxylate oxygen atom from each of two 3-methyl-2-thiophene carboxylate anions [Cu – O1 = 1.980 Å]. The remaining two carboxylate oxygen atoms of $[Cu(MTK)_2(MeFP)_2]$ which are bonded to the copper [Cu – O2 = 2.560 Å] bonds, lie at 57.43^O from the plane of CuO_2N_2 and create tetragonal-bipyramidal coordination. The copper(II) atom lies in the crystallographic center of symmetry.

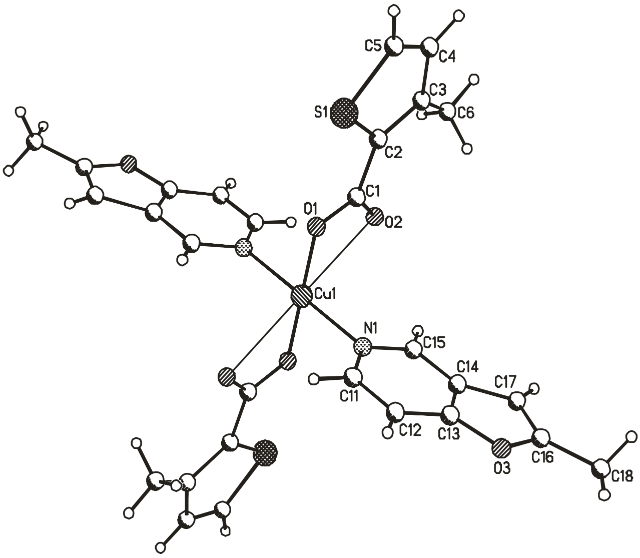


Fig. 2. The molecular structure of [Cu(MTK)$_2$(MeFP)$_2$] (complex **4**).

3.2 IR an electronic data

All the typical features of IR spectra are clearly compatible with the structural characteristics of the complexes under study. Some characteristic IR bands of the sodium salt NaMTK.H$_2$O as well as of Cu(II) complexes are given in Table 3.

The IR spectrum of complex **1** shows absorption bands in the region from 3200 to 3500 cm^{-1}. These bands correspond to the antisymmetric and symmetric OH stretch and confirm the presence of water.

The difference between the antisymmetric stretch and symmetric stretch (Δ) gives information on carboxylic bonding mode for the complexes after comparison with Δ values of compounds with ionic carboxylic groups (NAKAMOTO, 1997). The Δ values for the complexes **1** (152 – 211 cm^{-1}), **2** (175 – 234 cm^{-1}) and **3** (181 – 237 cm^{-1}) are comparable with Δ value for sodium salt (156 – 211 cm^{-1}) and suggested bridging mode of coordination carboxyl group. The considerable splitting of bands assigned to $\nu_s(COO^-)$ for complexes **1**, **2** and **3**, confirms that the MTK anion as a ligand is most probably coordinated via a bridging carboxyl group (Nakamoto, 1997). In these compounds, dimeric structure of acetate type known in other Cu(II) heterocyclic carboxylate (JAŠKOVÁ, *et al.*, 2007) is predicted.

The Δ values for the monomeric complexes **4** (188 – 261 cm^{-1}), **5** (174 – 247 cm^{-1}) and **6** (178 cm^{-1} – 261 cm^{-1}) are greater than for NaMTK·H$_2$O (156 – 211 cm^{-1}). That is rather typical for asymmetrically chelating carboxylate groups. However, in these cases, Δ values are comparable to those of unidentate complexes (NAKAMOTO, 1997). The suggested asymmetrically chelating O,O'-coordination of carboxylate groups for complexes under study is in agreement with the structure determined by X-ray analysis for complex **4**.

Table 3. Spectroscopic data[a] (in cm^{-1}) of Cu(II) complexes.

Compound	Infrared data			Electronic data	
	Carboxyl group				
	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	Δ[b]	Band I	Band II
NaMTK.H_2O	1573vs,br	1417vs 1364vs,br	156 - 209	-	-
$[Cu_2(MTK)_4(H_2O)_2]$ **1**	1574vs	1422vs 1373vs 1363vs	152 - 211	14 400	28 600sh
$[Cu_2(MTK)_4(FP)_2]$ **2**	1597vs	1422vs 1375vs 1363vs	175 - 234	13 700	28 000sh
$[Cu_2(MTK)_4(MeFP)_2]$ **3**	1600vs,br	1419vs 1375vs 1363vs	181 - 237	13 450	29 000sh
$[Cu(MTK)_2(MeFP)_2]$ **4**	1603s	1415vs,br 1342vs,br	188 - 261	17 500 13 500sh	-
$[Cu(MTK)_2(BFP)_2]$ **5**	1592vs	1418vs 1379vs 1345vs	174 - 247	17 400 13 900sh	-
$[Cu(MTK)_2(CF_3FP)_2]$ **6**	1601vs	1423vs 1380vs 1340vs	178 - 261	17500 13 800sh	

[a] vs – very strong; s – strong; m – medium; br – broad; sh – shoulder, [b]$\Delta = \nu_{as}(COO^-) - \nu_s(COO^-)$.

The solid state electronic spectra of complexes **1** – **3** show a broad absorption band (band I) in the visible region with a maximum from 13 450 cm^{-1} to 14 400 cm^{-1} (Table 3), which is assigned to a $d_{xy,yz} \rightarrow d_{x^2-y^2}$ transition (KATO, 1988). Moreover, the spectrum of complexes **1** – **3** displays a shoulder at about 28 500 cm^{-1} (band II). Band II has been assigned to a charge transfer absorption and is believed to be indicative of a dimeric complex, Finally, complexes **1** – **3** displays bands I and II in the usual range for Cu(II) compounds in a square-pyramidal CuO_4O' (complex **1**) or CuO_4N environment.

The solid state electronic spectra of all other copper(II) complexes under study exhibit a asymmetrical broad ligand field band with a maximum at about 17 500 cm^{-1}. This type of d–d spectra for complexes **4** – **6** is typical for tetragonally distorted octahedral copper(II) complexes (LEVER, 1984).

Some characteristic IR bands of the complexes Co(II) are given in Table 4. The IR spectrum for complex **7** shows absorption bands in the region from 3200 to 3500 cm^{-1} and confirms the presence of water. These bands are not present in other Co(II) complexes and confirm the absence of water. The Δ values for the complex **7** (151–214 cm^{-1}) are comparable with Δ values of NaMTK·H_2O (156 – 211 cm^{-1}) which suggests ionic mode of coordination of carboxylate group with hexaaquacobalt(II) cation and non-coordinated MTK anion. This manner of coordination is known (ZHANG and NG, 2005).

On the other hand, the Δ values from 169 to 241 cm^{-1} for complexes **8** – **11**, greater than for NaMTK·H_2O (156 – 211 cm^{-1}) are typical for an asymmetric chelating coordination of the carboxyl group of MTK anion.

Table 4. Spectroscopic data[a] (in cm^{-1}) of Co(II) complexes.

Compound	Infrared data			Electronic data	
	Carboxyl group				
	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	Δ^b	$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$	$^4T_{1g}(F)\rightarrow{}^4T_{2g}$
$NaMTK{\cdot}H_2O$	1573vs,br	1417vs 1364vs,br	156 - 209	-	-
$[Co(H_2O)_6](MTK)_2$ 7	1566vs	1415vs 1352s,br	151 - 214	20 000 21 300 sh	8 600
$[Co(MTK)_2(FP)_2]$ **8**	1589s	1420vs 1359vs	169 - 230	20 900sh 20 100 19 800sh	9400
$[Co(MTK)_2(MeFP)_2]$ **9**	1605vs	1420vs 1362vs	185 - 243	20 900sh 20 100	9300
$[Co(MTK)_2(BFP)_2]$ **10**	1593vs	1421vs 1358vs	172 - 235	20 950 20 100sh	9 500
$[Co(MTK)_2(CF_3FP)_2]$ **11**	1591	1422vs 1350	169 - 241	21 100	9 300

[a] vs – very strong; s – strong; m – medium; br – broad; sh – shoulder, [b] $\Delta = \nu_{as}(COO^-) - \nu_s(COO^-)$.

The electronic spectra (Table 4) of all the cobalt complexes are clearly consistent with tetragonally distorted octahedral structure. The electronic spectra consist of a band ν_1 assigned to the lowest energy transition $^4T_{1g}(F)\rightarrow{}^4T_{2g}$ in the near infrared and the band ν_3 in the visible near 20,000 cm^{-1}, which is assigned to the $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ transition.

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