# 4-Alkoxycarbonyl-2-(2-pyridyl)thiazoles and their complexes with Cu<sup>II</sup> and Co<sup>II</sup>. Molecular and crystal structure of copper 4-ethoxycarbonyl-2-(2-pyridyl)thiazole dichloride

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The first synthesis of ethyl 2-(2-pyridyl)thiazole-4-carboxylate (**2**) and bis[2-(2-pyridylthiazol-4-ylcarbonyloxy)ethyl] disulfide (**4**) is described. The complexation of compounds **2** and **4** with Cu<sup>II</sup>, Co<sup>II</sup>, and Ni<sup>II</sup> chlorides and perchlorates has been studied. Electrochemical behavior of the ligands and complexes obtained has been investigated by cyclic voltammetry and using rotating disk electrode, which allowed us to confirm the possibility for the ligand **4** and its complexes to be adsorbed on the surface of a gold electrode.

Key words: copper(II), cobalt(II), nickel(II), transition metal complexes, thiazoles, ligands, electrochemistry.

2-Aryl- and hetaryl-substituted imidazoles, oxazoles, and thiazoles belong to an important class of biologically active compounds.<sup>1-6</sup> It is known<sup>7</sup> that in many cases, a coordination with transition metal ions increases antiviral and antitumor activity of drugs. From this point of view, the thiazoles containing 2-pyridyl substituent at position 2 and capable of giving chelate five-membered metallacy-cles on complexation are of significant interest.

The copper(II) complexes with organic N,S-containing ligands capable of reversible reduction to the metal(I) complexes also attract attention as functional models of metalloenzymes and electroactive catalysts.<sup>8</sup> In this connection, it is desirable to obtain new complexes of this class, especially those containing additional disulfide groups remote from the chelating fragment and capable of providing "binding" of the metal complex to the surface of metallic electrodes.

Earlier,<sup>9</sup> we have synthesized a number of organic ligands of the 2-(2-pyridyl)-substituted benzothiazole series and shown that they are promising organic ligands for producing transition metal complexes. In the present work, we describe the synthesis of two structurally close ligands of the 2-(2-pyridyl)-substituted thiazole series and their complexes with Co<sup>II</sup>, Cu<sup>II</sup>, and Ni<sup>II</sup> salts. For one of the ligands under consideration with a disulfide fragment in the structure, a possibility of its adsorption on the surface of a gold electrode with subsequent complexation and formation of stable metallocomplex surfaces has been found.

## **Results and Discussion**

Synthesis of ligands and complexes. In the literature, there are described two basic methods for the preparation of 2-substituted thiazolecarboxylic acids: the oxidative dehydrogenation of thiazolidines<sup>10</sup> and the reaction of thioamides with bromo ketones<sup>11</sup>. On comparison of these methods with regard to the synthesis of 2-(2-pyridyl)-substituted thiazole, we found that attempted oxidation of ethyl ester of the corresponding substituted thiazolidine with *N*-bromosuccinimide (NBS) resulted in a complex mixture of products and failure to isolate the target compound. In contrast to this, the reaction of thioamide 1 (obtained by the reaction of 2-cyanopyridine with hydrogen sulfide) and ethyl 3-bromo-2-oxopropiolate leads to ethyl 2-(2-pyridyl)thiazole-4-carboxylate (2) in 74% yield (Scheme 1).

Ethanol or diethyl ether can also be used for the reaction with ethyl 3-bromo-2-oxopropiolate, however, DMF provides the highest yield of the product.

The hydrolysis of ester 2 to the corresponding acid 3 and subsequent esterification with di(2-hydroxyethyl) disulfide in the presence of DCC and DMAP afforded ligand 4 (Scheme 2).

To sum up, we synthesized ligand 4 capable of both to be adsorbed on the gold surface due to the presence of the disulfide fragment and to undergo complexation due to the presence of the donating pyridine and thiazole nitrogen atoms, as well as its more simple analog 2 with similar

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4 (45%)

coordinating fragment, but more soluble in most organic solvents due to the absence of a disulfide group.

The complexes were synthesized by a slow diffusion of a metallic salt solution in MeCN into the ligand solution in CH<sub>2</sub>Cl<sub>2</sub>. The salts CoCl<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·6H<sub>2</sub>O, and Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O were used in this method to obtain complexes for ligand **2**. When metallic chlorides are used (Scheme 3), there are formed complexes of the form M(**2**)Cl<sub>2</sub> (M = Cu (**5**), Co (**6**)); in the reaction with copper perchlorate, the composition of the complex corresponds to the molecular formula Cu(**2**)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (**7**). The structures of the complexes obtained were inferred from the X-ray diffraction data using compound **5** as an exam-

## Scheme 3

 $\mathbf{2} + MCl_2 \cdot 6H_2O \rightarrow M(\mathbf{2})Cl_2$ 

2 + Cu(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O → Cu(2)(ClO<sub>4</sub>)<sub>2</sub> 7 (24%)

In an effort to synthesize complexes of the ligand **2** with NiCl<sub>2</sub>·6H<sub>2</sub>O and Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, no crystalline complexes were obtained. Nevertheless, the complexation with nickel chloride was detected electrochemically (see below).

No crystalline complexes were obtained in such a way for the ligand **4**, however, the change in color of solution on mixing of the ligand **4** and metallic salt solutions suggests that complexation takes place in the solution. The complexation in this case is also confirmed by the results of electrochemical studies (see below).

The crystallographic data for the copper-containing complex 5, experimental details, and refining parameters of the structure are given in Table 1. Molecular structure of compound 5 is shown in Fig. 1, selected bonds distances and bond angles are given in this Figure captions. The copper atom in the complex 5 has a tetrahedral ligand surrounding and is coordinated by the nitrogen atoms of



Fig. 1. Molecular structure of complex 5. Selected bond distances (Å) and bond angles (deg): Cu(1)-N(1) 2.002(4); Cu(1)-N(2) 2.025(4); Cu(1)-Cl(1) 2.198(2); Cu(1)-Cl(2) 2.222(2); N(1)-Cu(1)-N(2) 80.3(2); N(1)-Cu(1)-Cl(1) 148.1(2); N(2)-Cu(1)-Cl(1) 98.5 (1); N(1)-Cu(1)-Cl(2) 99.2(1); N(2)-Cu(1)-Cl(2) 136.7(2); Cl(1)-Cu(1)-Cl(2) 102.9(1).

Table	1.	Crystall	ographic	data,	experimental	l details,	and	refin-
ing par	rar	neters fo	or the str	ucture	of compound	15		

Parameter	Value
Molecular formula	$C_{11}H_{10}Cl_2CuN_2O_2S$
Molecular weight	368.71
T/K	296(2)
Wavelength/Å	0.71073
Type of crystal	Green needles
Size of crystal/mm	$0.6 \times 0.2 \times 0.1$
Crystal system	Triclinic
Space group	<i>P</i> -1
Parameters of unit cell	
a/Å	7.7230(15)
b/Å	8.5480(17)
c/Å	11.638(2)
α/deg	94.93(3)
β/deg	106.04(2)
γ/deg	108.13(3)
$V/Å^3$	689.2(3)
Ζ	2
$d_{\rm calc}/{\rm g~cm^{-3}}$	1.777
Absorption coefficient/mm <sup>-1</sup>	2.120
<i>F</i> (000)	370
Range of $\theta/deg$	1.85-29.96
Ranges of reflection indices	$0 \le h \le 10,$
	$-12 \le k \le 11,$
	$-15 \le l \le 15$
Number of measured/	4274/
independent reflections	3996
$(R_{\rm int})$	(0.0808)
Number of refining variables	173
Reliability on $F^2$	0.990
<i>R</i> -Factors $(I > 2\sigma(I))$	
$R_1$	0.0583
$wR_2$	0.0958
<i>R</i> -Factors (on all the data)	
$R_1$	0.2402
wR <sub>2</sub>	0.1325

the pyridine and thiazole rings and two chloride anions. The thiazole and pyridine rings of the molecule are virtually coplanar.

Electrochemical study of compounds 2 and 4 and their complexes. Ligands 2 and 4 and their complexes were studied by cyclic voltammetry (CVA) and rotating disk electrode method (RDE) in DMF solutions on a glass-filled carbon (GFC), Pt and Au electrodes in the presence of 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> as an indifferent electrolyte. The potentials of electrochemical oxidation and reduction measured relatively to Ag|AgCl|KCl(sat.) are given in Table 2. Cyclic voltamograms are given in Fig. 2.

The reduction of ligand **2** (GFC electrode) takes place in two steps, the first of which ( $E_{pc} = -1.79/-1.72$  V) is reversible (see Fig. 2, *a*). According to the data of quantum chemical calculations (*ab initio* SCF method PM3<sup>12</sup> including into the Hyperchem program package; optimi-

**Table 2.** Oxidation  $(E^{Ox})$  and reduction  $(E^{Red})$  potentials for ligands **2** and **4** and their complexes measured by the CVA and RDE methods (rel. Ag|AgCl|KCl sat.) on GFC(Au) electrode in DMF in the presence of 0.1 *M* Bu<sub>4</sub>NClO<sub>4</sub> <sup>*a*</sup>

Com-	$E_{\rm pc}^{\rm Red}$	$E_{1/2}^{\text{Red}}$	$E_{\rm pc}^{\rm Ox}$	$E_{1/2}^{Ox}$
pound		V		
2	-1.79/-1.72	-1.80 (1)	_	_
	-2.12 <sup>b</sup>			
5	0.44/0.52 <sup>c</sup>	0.42 (1) <sup>c</sup>	1.18	1.30(2)
	-1.80	-1.81 (1)		
	-2.33			
6	-1.15/0.08	$-1.12(1.3)^{d}$	1.28	1.23(2)
	-1.80/-1.72	-1.85(1)		
7	$0.06/0.12^{c}$	$0.07(0.9)^{c}$	_	_
	-0.34/0.10	-0.34(0.9)		
	-1.76/-1.70	-1.79(1.8)		
$2 + \text{NiCl}_2$	-1.23/0.02	$-1.12(1.6)^{d}$	1.16	1.17 (2)
•6H <sub>2</sub> O	-1.79/-1.72	-1.83(1)		
(in situ)	,			
4-1.56	-1.56 (1	) $1.16^{b}$	1.16 C	2)
	-2.07/-2.00	-1.87(1)	(	-,
	-2.63	(-)		
$4^{e}$ + CuCla	$0.30/0.38^{\circ}$	_	0.93	_
•6H_0	-0.85	1.09	0.95	
01120	-1.97 b	1.09		
$A^{e} + \text{NiCl}$	-0.85	- 1.06		
	1 28/0 27	-1.00		
·0H <sub>2</sub> O	-1.20/0.27	1.57		
	-1.91 °			

<sup>*a*</sup>  $E_{pc}$ , potentials of cathode peaks (200 mV s<sup>-1</sup>)/potentials of reverse peaks;  $E_{1/2}$ , potentials of half-wave measured by the RDE method (2800 rpm). The number of electrons determined by comparison with the height of a one-electron wave of the oxidation of ferrocene is given in parentheses.

<sup>b</sup> Peak of low intensity.

<sup>*c*</sup> Initial potential, 0.7 V.

<sup>*d*</sup> In the experiments on RDE, the electrode processes are complicated by the covering of the surface with a zero-valence metal  $(M^0)$ , the electroreduction takes place on the modified surface, that leads to a drop in the current and does not allow one to precisely determine the number of transmitted electrons. <sup>*e*</sup> Ligand **4** adsorbed on the surface of Au electrode.

zation of molecular geometry was made with the set gradient of convergence no more than 10 cal  $Å^{-1}$  mol<sup>-1</sup>), both the HOMO and the LUMO of the ligand **2** are mainly localized on the thiazole fragments. Cosequently, the initial oxidation and reduction should occur at the cyclic fragment. However, no peaks are observed in the region of oxidation: apparently, the oxidation of ligand **2** should

The study of electrochemical reduction of the coppercontaining complex 5 using CVA exhibits a one-electron quasi-reversible reduction at the copper atom (Scheme 4) at  $E_{pc} = 0.44$  V (see Fig. 2, b). The intermediate containing Cu<sup>I</sup> is stable when stud-

occur at more anodic potentials.

The intermediate containing  $Cu^{I}$  is stable when studied on a GFC electrode. This fact is confirmed by the



**Fig. 2.** Cyclic voltamgrams (GFC electrode (unless other electrode material is specified), DMF, 0.1 *M* Bu<sub>4</sub>NClO<sub>4</sub>): *a*, ligand **2** ( $10^{-3}$  mol L<sup>-1</sup>), *b*, complex **5** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *c*, complex **5** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *Au* electrode), *d*, complex **7** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *e*, complex **7** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *g*, ligand **4** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *h*, ligand **4** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *h*, ligand **4** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *h*, ligand **4** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *h*, ligand **4** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *h*, ligand **4** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *h*, ligand **4** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *h*, ligand **4** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *h*, ligand **4** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *h* ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *h*, ligand **4** ( $5 \cdot 10^{-4}$  mol L<sup>-1</sup>), *h* ( $5 \cdot 10^{-4}$  mol

Scheme 4

$$\operatorname{Cu^{II}(2)Cl}_{2} \xrightarrow{+e}_{-e} \operatorname{Cu^{I}(2)Cl}_{2}$$

absence of the peak of oxidative desorbtion of metallic copper from the electrode on the reverse scan of the CVA curve even after the potential  $E_{\rm pc} = -2.0$  V was reached. In addition, the peak corresponding to the reduction of the ligand is irreversible for the complex **5**, in contrast to the first cathode peak of the free ligand (see Table 2, Fig. 2, *b*).

When the study was carried out on an Au electrode, similarly to the GFC electrode, the complex **5** is stable in solution unlike, for example, Cu(creat)<sub>2</sub>Cl<sub>2</sub> (creat means creatinine (2-amino-1-methyl-1,5-dihydro-4*H*-imidazol-4-one)),<sup>13</sup> the electroreduction of which is preceded by decomposition of the complex to the starting components. However, it should be noted that on the metallic electrodes (to a lesser extent, on the Pt electrode and to a greater, on the Au electrode), a disproportionation of the intermediate Cu<sup>I</sup>(2)Cl<sub>2</sub> (obtained by a one-electron reduction) to the complex **5** and Cu<sup>0</sup> compound takes place. The copper(0) complex apparently decomposes with the liberation of metallic copper (Scheme 5), that leads to the cathode shift of the reoxidation peak and increase in its intensity (see Table 2, Fig. 2, c).

#### Scheme 5

Such disproportionation processes on Pt and Au electrodes were also observed during electroreduction of the complex 7. On the GFC electrode, the first peak of reduction, as for 5, is a one-electron and quasi-reversible, that testifies the stability of the copper(1) complex. But after the second cathode peak ( $E_{pc} = -0.34 \text{ V}, \text{Cu}^{\text{I}}(2)(\text{CIO}_4)_2 \rightarrow Cu^0(2)(\text{CIO}_4)_2)$  on the reverse scan of the volt-ampere curve, the peak of the desorption of metallic copper is observed ( $E_{pa} = 0.08 \text{ V}$ ; see Table 2, Fig. 2, *d*, *e*). Thus, the stability of complex 7 containing perchlorate ions is lower than the stability of complex 5 having chloride ions in its structure.

On the CVA curves of the complex with CoCl<sub>2</sub> (6), there is additional peak of reduction at  $E_{pc} = -1.15$  V as compared to the ligand, after which the peak of the desorption of metallic cobalt is observed on the reverse scan

of the volt-ampere curve. This testifies that a two-electron reduction at the metal initially takes place, the zero-valent cobalt complex obtained is unstable and decomposes to the ligand **2** and metallic cobalt. The second reversible cathode peak corresponds to the reduction of the free ligand (see Fig. 2, f). The oxidation of complex **6** occurs at  $E_{pa} = 1.28$  V, that corresponds to the reduction of chloride anions.

The complex of ligand **2** with NiCl<sub>2</sub> was obtained only in solution *in situ*. The mixing of ligand **2** and NiCl<sub>2</sub>•6H<sub>2</sub>O in DMF solution exhibits the change of the solution color and the emergence on the voltamograms of irreversible cathode peak of the complex reduction at  $E_{pc} = -1.23$  V instead of the peak of NiCl<sub>2</sub> reduction at  $E_{pc} = -1.32$  V (see Table 2). The CVA curves of this complex on the whole are similar to those for complex **6**, that testifies basically the same mechanism of electroreduction for both complexes (see Table 2).

To sum up, the complexes of ligand **2** with Co<sup>II</sup> and Ni<sup>II</sup> chlorides under study undergo a two-electron reduction "at the metal" in the first step and decompose with the liberation of metallic cobalt or nickel and the free ligand; the copper-containing complexes **5** and **7** in the first step undergo a one-electron reduction to the stable copper(1) complexes. After the second cathodic one-electron process, the complex **7** containing perchlorate ions decomposes with the liberation of metallic copper and the free ligand, whereas the complex **5** does not undergo destruction under these conditions (on the GFC electrode). On the Pt and Au electrodes, the Cu<sup>I</sup>-containing intermediates disproportionate at a noticeable rate.

The reduction of ligand **4** (GFC electrode) occurs at less negative potentials ( $E_{pc} = -1.56$  V) than the reduction of ligand **2** (see Fig. 2, g).

According to the data of quantum chemical calculations, both the HOMO and the LUMO of ligand 4 are localized mainly on the disulfide fragment, in contrast to ligand 2 where they were localized on the benzothiazole fragments. Apparently, the irreversible reduction of ligand 4 occurs initially at the disulfide fragment to form the thiolate anions. The second reversible peak of the reduction is observed at  $E_{\rm pc} = -2.07$  V. When the ligand **4** is studied on the Au electrode, already the first scans exhibit a new peak at  $E_{pc} = -0.88$  V (see Table 2, Fig. 2, h) apparently related to the reduction of the fragment Au-S (see Refs 14–16) with the simultaneous decrease in the intensity of the cathodic peak, which corresponds to the electroreduction of the S–S bond. If the electrode is kept in a solution of this ligand for 20 h, the peak at  $E_{\rm pc} = -$ 1.56 V completely disappears. Apparently, this is due to the fact that the disulfide fragment present in the starting molecule disappears during adsorption because of the cleavage of the S-S bond with the generation of the Au-S bond and the formation of a monolayer.

If the Au electrode modified with ligand 4 is kept in a solution of metallic salt (Cu<sup>2+</sup>, Ni<sup>2+</sup>) for 30 min and

washed followed by recording voltamgrams in a pure solution of the electrolyte, then the CVA curves in both cases exhibit peaks identical to those observed for the corresponding complexes with a model ligand **2**. This fact confirms the formation on the surface of coordination compounds of similar structure.

In conclusion, there have been isolated  $Cu^{II}$  and  $Co^{II}$  complexes with 2-(2-pyridyl)thiazole-4-carboxylic esters including ester **4** containing a disulfide group remote from the chelating 2-pyridylthiazole fragment; the complexation of this ligand with Ni<sup>II</sup> in solution has been detected electrochemically. For the ligand **4**, a possibility of its adsorption on the surface of Au electrode has been demonstrated with subsequent formation of metallocomplex surfaces. Further, we plan to study possible catalytic activity of the complexes synthesized in the reactions of oxidation and electro-induced reduction.

## Experimental

The reaction course was monitored by TLC on Silufol plates with a bound layer of silica gel. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian—Mercury-400 or Bruker—Evance-400 spectrometers (400 MHz) at 25 °C in deuterated chloroform and DMSO-d<sub>6</sub>. IR spectra were recorded on a UR-20 spectrometer in Nujol. Mass spectra were recorded on a Finnigan MAT SSQ 7000 GC-MS spectrometer (70 eV, an OV-I quartz capillary column (25 m), the temperature mode: 70 °C (2 min)— 20 °C min<sup>-1</sup>—280 °C (10 min)).

X-ray diffraction analysis was performed on a CAD-4 monocrystal automatic diffractometer (a graphite monochromator,  $\lambda$ (Mo-K $\alpha$ ) = 0.71073 Å,  $\omega$ -scanning). The structure was decoded by the direct method (SHELXS-97)<sup>17</sup> and refined in the fullmatrix anisotropic least squares merhod on  $F^2$  for all nonhydrogen atoms (SHELXL-97).<sup>18</sup> All the hydrogen atoms were localized objectively and refined in the isotropic approximation.

A PI-50-1.1 potentiostate was used for the electrochemical studies, which was connected to a PR-8 programator. A glass-filled carbon (d = 2 mm), platinum (d = 3 mm), and gold (d = 2 mm) disks were used as working electrodes, 0.1 *M* solution of Bu<sub>4</sub>NClO<sub>4</sub> in DMF as a background electrolyte, Ag/AgCl/KCl (sat.) as a comparison electrode, platinum plate as an auxiliary electrode. The surfaces of working electrodes were polished with the powder of aluminum oxide with particle <10 µm in size (Sigma—Aldrich). The potential scanning rate in the CVA method was 200 mV s<sup>-1</sup>, in the RDE method, 20 mV s<sup>-1</sup>. The potentials are given with allowance for the *iR*-compensation. The number of transmitted electrons in the redox-processes was determined by comparison of the maximum wave current value in the experiments on the RDE with the current of a one-electron oxidation of ferrocene taken in the same concentration.

All the measurements were performed under dry argon; samples were dissolved in a degassed solvent. DMF (pure grade) was purified by stirring over freshly calcined  $K_2CO_3$  for 4 days with subsequent distillation *in vacuo* first over  $P_2O_5$ , then, over anhydrous CuSO<sub>4</sub>.

**2-Pyridinethiocarboxamide (1)** was obtained according to the modified procedure described earlier.<sup>19,20</sup> A solution of 2-pyridinecarbonitrile (10 g, 0.096 mol) in benzene (50 mL) and

a solution of Na<sub>2</sub>S·9H<sub>2</sub>O (0.42 g) and TEBAC (0.35 g) in water (14 mL) were placed into a 250-mL one-neck thick-wall flask equipped with a magnetic stirring bar, the flask was filled with dry H<sub>2</sub>S and heated to 70 °C for 3 h with vigorous stirring on a water bath in the flow of H<sub>2</sub>S. A precipitate of thioamide formed was filtered off and recrystallized from EtOH to obtain thioamide 1 (49.56 g, 72%) as yellow crystals. M.p. 138–140 °C (*cf.* Refs 19 and 20: m.p. 137–138 °C). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>), δ: 9.56 (br.s, 1 H, NH); 8.71 (d, 1 H,  $\alpha$ -Py, J = 7.8 Hz); 8.52 (d, 1 H,  $\beta$ '-Py, J = 4.5 Hz); 8.11 (br.s, 1 H, NH); 7.84 (td, 1 H,  $\beta$ -Py,  $J_1$  = 7.8 Hz,  $J_2$  = 1.8 Hz); 7.45 (dd, 1 H,  $\gamma$ -Py,  $J_1$  = 4.51 Hz,  $J_2$  = 1.0 Hz).

**Ethyl 2-(2-pyridyl)thiazole-4-carboxylate (2).** Ethyl 3-bromo-2-oxopropiolate  $(1.41 \text{ g}, 7.2 \cdot 10^{-3} \text{ mol})$  was added to thioamide 1 (1 g, 7.2 · 10<sup>-3</sup> mol) in DMF (10 mL). The mixture was heated for 3 h on a water bath at 100 °C with stirring. The solvent was evaporated under reduced pressure to obtain ester 2 (1.19 g, 74%) as a dark brown oil. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>),  $\delta$ : 8.63 (d, 1 H, Py- $\alpha$ -H, *J* = 4.9 Hz); 8.35 (d, 1 H, Py- $\beta$ '-H, *J* = 7.9 Hz); 8.27 (s, 1 H, thiazole); 7.84 (d, 1 H, Py- $\beta$ -H, *J* = 6.2 Hz); 7.37 (t, 1 H, Py- $\gamma$ -H, *J* = 6.2 Hz); 4.47 (q, 2 H, CH<sub>2</sub>, *J* = 7.2 Hz); 1.45 (t, 3 H, Me, *J* = 7.1 Hz). IR, v/cm<sup>-1</sup>: 1730 (C=O).

**2-(2-Pyridyl)thiazole-4-carboxylic acid (3).** Potassium hydroxide (0.13 g,  $2.33 \cdot 10^{-3}$  mol) in EtOH—H<sub>2</sub>O (1 : 1, 10 mL) was added to a solution of ester **2** (0.36 g,  $1.56 \cdot 10^{-3}$  mol) in the same mixture of solvents (10 mL) followed by stirring for 3 h and addition of 1 *M* HCl to pH = 2. A precipitate was filtered off to obtain acid **3** (0.217 g, 68%) as light brown crystals. M.p. 224—226 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 8.67 (d, 1 H, Py- $\alpha$ -H, J = 4.7 Hz); 8.57 (s, 1 H, thiazole); 8.16 (d, 1 H, Py- $\beta$ '-H, J = 7.9 Hz); 7.84 (d, 1 H, Py- $\beta$ -H, J = 6.2 Hz); 7.37 (t, 1 H, Py- $\gamma$ -H, J = 6.2 Hz). MS, m/z ( $I_{rel}$  (%)): 208 [MH]<sup>+</sup> (73).

**Bis**[2-(2-pyridylthiazol-4-ylcarbonyloxy)ethyl] disulfide (4). Di(2-hydroxyethyl) disulfide (0.08 g,  $4.8 \cdot 10^{-4}$  mol), dicyclohexylcarbodiimide (0.22 g,  $9.7 \cdot 10^{-4}$  mol), and 4-dimethylaminopyridine (0.02 g,  $1.6 \cdot 10^{-4}$  mol) were added to a solution of acid **3** (0.2 g,  $9.7 \cdot 10^{-4}$  mol) in dichloromethane (20 mL) followed by stirring for 11 h. The solvent was evaporated at reduced pressure. The residue was recrystallized from EtOH. The yield was 0.115 g (45%). M.p. >300 °C. Found (%): C, 49.99; H, 3.30; N, 10.31. C<sub>22</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>S<sub>4</sub>. Calculated (%): C, 49.81; H, 3.40; N, 10.57. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>), δ: 8.64 (d, 1 H, Py-α-H, J = 7.0 Hz); 8.62 (s, 1 H, thiazole); 8.14 (d, 1 H, Py-β'-H, J = 7.0 Hz); 8.00 (d, 1 H, Py-β-H, J = 7.0 Hz); 7.55 (t, 1 H, Py-γ-H, J = 7.1 Hz); 4.58 (t, 2 H, CH<sub>2</sub>CO, J = 6.2 Hz); 3.22 (t, 2 H, CH<sub>2</sub>S, J = 6.2 Hz).

Preparation of complexes with ligand 2 (general procedure). A solution of thiazole 2 (0.045 g, 0.085 mmol) in dichloromethane (1 mL) was placed into a test-tube followed by a slow (along the test-tube wall) addition to it of acetonitrile (200  $\mu$ L) so as to form a two-phase system. Then, a solution of metallic salt (0.085 mmol) in acetonitrile (1 mL) was slowly added to it. The reaction mixture was tightly capped and left to form crystals (for 2–3 days). The solvent was decanted from the crystals formed, which were dried in air.

Copper 4-ethoxycarbonyl-2-(2-pyridyl)thiazole dichloride (5). The yield was 0.0054 g (18%), dark green crystals. Found (%): C, 36.23; H, 2.73; N, 7.64.  $C_{11}H_{10}Cl_2CuN_2O_2S$ . Calculated (%): C, 36.82; H, 2.79; N, 7.81.

**Cobalt 4-ethoxycarbonyl-2-(2-pyridyl)thiazole dichloride (6).** The yield was 0.0066 g (22%), dark blue crystals. Found (%): C, 36.40; H, 2.61; N, 7.64.  $C_{11}H_{10}Cl_2CoN_2O_2S$ . Calculated (%): C, 36.26; H, 2.75; N, 7.69.

Copper bis[4-ethoxycarbonyl-2-(2-pyridyl)thiazole] diperchlorate (7). The yield was 0.0066 g (22%), dark red crystals. Found (%): C, 39.23; H, 3.01; N, 8.18.  $C_{22}H_{20}Cl_2CuN_4O_{12}S_2$ . Calculated (%): C, 39.61; H, 3.00; N, 8.40.

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