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Conversion of 2-thiohydantoins and their derivatives to the corresponding hydantoins in the processes of complexation reactions with copper(II) chloride dihydrate

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ABSTRACT

The treatment of 5-pyridylmethylene-substituted 2-thiohydantoins or 2-alkylthio-3,5-dihydro-4H-imidazole-4-ones with $CuCl_2 2H_2O$ affords the mononuclear or polymeric copper(II) complexes of the corresponding hydantoins. A presumable mechanism of hydantoin moiety formation involves Lewis acid catalyzed nucleophilic substitution of a sulfur-containing leaving group in the organic ligand by a water molecule from $CuCl_2 2H_2O$. The copper complexes $Cu(L^1\text{-}H)Cl(H_2O)$ (**7**; L^1 = (Z)-3-allyl-5-(pyridine-2-ylmethylene)imidazole-2,4(4*H*)-dione) and $Cu(L^2\text{-}H)_2$ (**9**; L^2 = Z)-3-allyl-5-(5′-bromo-pyridine-2-ylmethylene)imidazole-2,4(4*H*)-dione) were characterized by X-ray diffraction.

1. Introduction

Hydantoins and their derivatives have attracted attention for their antidiabetic [1], antiarrhythmic [2] anticonvulsant [3], antitumor, antiangiogenic and antimetastatic [4], serotonin and fibrinogen receptor antagonistic [5] and aldose reductase inhibitory [6] activities. Hydantoin and related moieties are also found in many bioactive natural products [7].

Desulfurization of 2-thiohydantoin for its conversion to the corresponding hydantoins is a known method for the synthesis of therapeutically relevant compounds. Existing methods for desulfurization of 2-thiohydantoins include hydrolysis catalyzed by protonic [8] and Lewis acids [9] or by bases [10], use of hydrogen peroxide in combinations with different co-reagents ((DMF)/CH_3COOH [11], $NaHCO_3/H_2O$ [12], pyridine [13], ROH [14]), NaOMe/MeI/DMF [15], tetrabutylammonium periodate [16], $Hg(OAc)_2$ with a microwave [17], HgO in AcOH [18] or nitrous dioxide [19]. For another group of 2-thiohydantoins, the desulfurization methods include the initial S-alkylation of 2-thiohydantoin followed by treatment with HCl in EtOH or H_2O [20], MeONa, AcONa or NH_3 [10,21], and $Hg(OAc)_2$ with a microwave [22]. Most of these methods mean the use of hazardous chemicals, oxidizing agents or strong acids.

Hydantoins, like many drugs, have metal binding sites that can interact with metals found in serum [23]. It is known that in some cases the biological activity and toxicity of organic compounds are increased by the presence of metal ions, which would be expected to be the case if the chelate is the active form of the drug [24]. The preparation, structure and properties of some hydantoin complexes with Ag(I), Au(I), Au(III), Cu(II), Co(II), Ni(II), Pd(II), Pt(II), Pt(IV), Mn(II), Cd(II), Hg(II), Sb(V), Re(V), Sn(IV) and Ti(IV) have been reported [23,25].

We recently synthesized a series of mono- and binuclear complexes of Cu(I) and Cu(II) with 5-(pyridylmethylene)- [26] and 5-(imidazoleylmethylene)-2-thiohydantoins [27] and demonstrated that the primary product of the reaction of (4Z)-2-thioxo-4-[(1-methyl-1H-imidazole-2-yl)methylene]-1-(n-propyl)-imidazole-5(4H)-one with $CuCl_2 2H_2O$ is the hydantoin-containing copper(II) complex, which apparently forms as a result of copper ion-mediated nucleophilic substitution of a ligand sulfur atom by a water molecule from $CuCl_2 2H_2O$. In this work we describe the synthesis of novel hydantoin-containing copper(II) complexes from 5-(pyridylmethylene)-2-thiohydantoin or 2-alkylthio-5-(pyridylmethylene)-3,5-dihydro-4H-imidazole-4-one as the result of their reactions with copper(II) chloride dihydrate.

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2. Experimental

All materials were obtained from commercial sources and used as received. The melting points are uncorrected. ^{1}H NMR spectra were recorded on a Varian-XR-400 recorder (400 MHz for ^{1}H). The IR spectra in Nujol were recorded on a Perkin-Elmer 1430 spectrophotometer.

2.1. 5-Substituted 2-thiohydantoins **3**–**5** (typical procedure)

Pyridine-2-carbaldehyde or 5-bromo-pyridine-2-carbaldehyde (1 eq) was added to a solution of thiohydantoin **1** or **2** (1 eq) in 2% KOH solution in EtOH, and this mixture was stirred at room temperature for 3 h. The precipitate that formed was filtered off and then suspended in water. Concentrated HCl solution was added under stirring to bring the pH to 7. The precipitate was filtered off, washed with EtOH, diethyl ether and dried in air.

2.1.1. (5Z)-2-Thioxo-3-allyl-5-[(pyridine-2-yl)methylene]-imidazole-4(4H)-one (**3**)

0.16 g (93%) of compound **3** were obtained as a result of the reaction between 0.1 g (0.64 mmol) thiohydantoin **1** and 0.068 g (0.64 mmol) pyridine-2-carbaldehyde. M.p. 178 °C. ^{1}H NMR (DMSO-d_6): 4.41 (d, 2H, CH_2, J = 5.08 Hz), 5.14 (m, 2H, =CH_2), 5.86 (dd, 1H, =CH, J_1 = 5.36 Hz, J_2 = 10.55 Hz), 6.77 (s, 1H, =CH), 7.40 (m, 1H, Py), 7.76 (d, 1H, Py, J = 7.51 Hz), 7.90 (dt, 1H, Py, J_1 = 1.46 Hz, J_2 = 7.51 Hz), 8.76 (d, 1H, Py, J = 3.14 Hz), 11.76 (s, 1H, –NH). IR, ν/cm^{-1}: 3311, 1728, 1662, 1455, 1428. *Anal.* Calc. for $C_{11}H_{11}N_3OS$ (**3**): C, 58.78; H, 4.49; N, 17.14. Found: C, 58.67; H, 4.63; N 17.09%.

2.1.2. (5Z)-2-Thioxo-3-allyl-2-[(5′-bromo-pyridine-2-yl)methylene]-imidazole-4(4H)-one (**4**)

0.34 g (78%) of compound **4** were obtained as a result of the reaction between 0.2 g (1.28 mmol) thiohydantoin **1** and 0.23 g (1.28 mmol) 5-bromo-pyridine-2-carbaldehyde. M.p. 189–191 °C. ^{1}H NMR (DMSO-d_6): 4.41 (d, 2H, CH_2, J = 5.51 Hz), 5.13 (dd, 2H, =CH, J_1 = 10.00 Hz, J_2 = 15.39 Hz), 5.85 (dt, 1H, =CH, J_1 = 5.51 Hz, J_2 = 11.93 Hz), 6.73 (s, 1H, =CH), 7.16 (d, 1H, Py, J = 8.08 Hz), 8.15 (d, 1H, Py, J = 8.08 Hz), 8.82 (s, 1H, Py), 11.70 (bs, 1H, –NH). IR, ν/cm^{-1}: 3240, 1730, 1680, 1460. *Anal.* Calc. for $C_{11}H_{10}N_3OBrS$ (**4**): C, 42.31; H, 3.21; N, 13.46; S, 10.26. Found: C, 42.38; H, 3.31; N 13.50; S, 10.19%.

2.1.3. (5Z)-2-Thioxo-3-phenyl-2-[(5′-bromo-pyridine-2-yl)methylene]-imidazole-4(4H)-one (**5**)

0.98 g (99%) of compound **5** were obtained as a result of the reaction between 0.5 g (2.6 mmol) of thiohydantoin **2** and 0.48 g (2.6 mmol) 5-bromo-pyridine-2-carbaldehyde. M.p. 265–267 °C. ^{1}H NMR (DMSO-d_6): 6.81 (s, 1H, =CH), 7.37–7.69 (m, 5H, Ph), 7.77 (d, 1H, Py, J = 6.18 Hz), 8.18 (d, 1H, Py, J = 6.18 Hz), 8.88 (s, 1H, Py), 11.81 (bs, 1H, –NH). IR, ν/cm^{-1}: 3262, 1729, 1654. *Anal.* Calc. for $C_{16}H_{11}N_3OBrS$ (**5**): C, 51.47; H, 2.94; N, 11.26; S, 8.58. Found: C, 51.29; H, 2.81; N 11.55; S, 8.66%.

2.2. (5Z,5′Z)-2,2′-(ethane-1,2-diylsulfanyldiyl)bis[5-(5′-bromo-pyridine-2-ylmethylene)-3-allyl-3,5-dihydro-4H-imidazole-4-one] (**6**)

1,2-Dibromoethane (0.06 g, 0.31 mmol) was added to a stirred mixture of compound **4** (0.2 g, 0.62 mmol) and dried K_2CO_3 (0.9 mmol) in 50 ml DMF. The resulting mixture was stirred for 2 h at 0 °C, then for 2 h at room temperature. After this time 50 ml of water was added. The formed precipitate was collected, washed with water, diethyl ether and dried in air. Yield 0.16 g (62%). M.p. 230–232 °C. ^{1}H NMR ($CDCl_3$): 1.58 (s, 1H, CH_2), 4.27 (d, 2H, CH_2, J = 5.97 Hz), 5.30 (t, 2H, =CH, J = 10.62 Hz), 5.85 (dt, 1H, =CH, J_1 = 5.97 Hz, J_2 = 15.60 Hz), 7.10 (s, 1H, =CH), 7.76 (dd, 1H, Py, J_1 = 2.61 Hz, J_2 = 8.53 Hz), 8.57 (d, 1H, Py, J = 8.53 Hz), 8.72 (d, 1H, Py, J = 2.60 Hz). IR, ν/cm^{-1}: 3031, 1718, 1637, 1488. *Anal.* Calc. for $C_{26}H_{22}N_6O_2Br_2S_2$ (**6**): C, 46.29; H, 3.26; N, 12.46; S, 9.49. Found: C, 46.17; H, 3.24; N 12.29; S, 9.23%.

2.3. Synthesis of the coordination compounds (typical procedure)

A concentrated solution of ligand **3**, **5** or **6** in 2 ml of CH_2Cl_2 and an equimolar amount of $CuCl_2 2H_2O$ in 2 ml of EtOH were carefully mixed and the reaction mixture, placed in an open test-tube, was left at room temperature in a tightly capped vessel containing 10 ml of diethyl ether. After two days, crystals of the hydantoin complexes **7**–**9** were formed as a result of the slow diffusion of the ether vapor into the solution. The formed crystals were filtered off, washed with small portions of Et_2O and dried in air.

2.3.1. (Z)-3-allyl-5-(pyridine-2-ylmethylene)imidazole-2,4(4H)-dione copper(II) chloride hydrate (**7**)

Dark-yellow very thin plates (0.02 g, 36%) were obtained from 0.022 g (0.055 mmol) of ligand 3 and 0.007 g (0.055 mmol) of $CuCl_2 2H_2O$. M.p. 154–156 °C. IR, ν/cm^{-1}: 3420, 1720, 1655, 1578, 1470. *Anal.* Calc. for $C_{12}H_{12}N_3O_3ClCu$ (**7**): C, 41.75; H, 3.50; N, 12.17. Found: C, 41.64; H, 3.43; N 12.02%.

2.3.2. (Z)-3-phenyl-5-(5′-bromo-pyridine-2-ylmethylene)imidazole-2,4(4H)-dione copper(II) chloride hydrate (**8**)

Black needles (0.011 g, 37%) were obtained from 0.02 g (0.055 mmol) of ligand **5** and 0.007 g (0.055 mmol) of $CuCl_2 2H_2O$. M.p. 215–217 °C. IR, ν/cm^{-1}: 3419, 1718, 1645. *Anal.* Calc. for $C_{15}H_{11}N_3O_3BrClCu$ (**7**): C, 39,15; H, 2.41; N, 9.13. Found: C, 39.33; H, 2.11; N 9.03%.

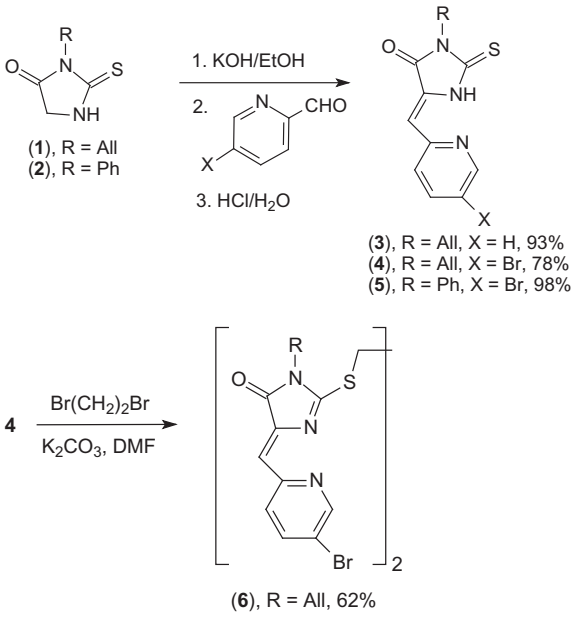
2.3.3. Bis[(Z)-3-allyl-5-(5′-bromo-pyridine-2-ylmethylene)imidazole-2,4(4H)-dione] copper(II) (**9**)

Black spiky prisms (0.032 g, 62%), were obtained from 0.05 g (0.074 mmol) of ligand 6 and 0.02 g (0.15 mmol) of $CuCl_2 2H_2O$. M.p. >300 °C. IR, ν/cm^{-1}: 3450, 3087, 1747, 1656, 1643, 1487, 1454. *Anal.* Calc. for $C_{24}H_{14}N_6O_4Br_2Cu$ (**9**): C, 42.78; H, 2.09; N, 12.47. Found: C, 43.09; H, 2.44; N 12.66%.

3. Results and discussion

3.1. Synthesis of the ligands and the complexes

The 3-substituted 2-thioxotetrahydro-4H-imidazole-4-ones **1** and **2** were prepared according to literature procedures [20b]. 5-(Pyridine-2-ylmethylene)-2-thiohydantoins **3**–**5** were synthesized by a base-catalyzed condensation reaction between 2-thiohydantoin **1** or **2** and the corresponding pyridinecarbaldehydes, as shown in Scheme 1. 2,2′-(Ethane-1,2-diylsulfanyldiyl)bis(5-(5′-bromo-pyridine-2-ylmethylene)-3,5-dihydro-4H-imidazole-4-one **6** was obtained by alkylation of 2-thiohydantoin **4** with 1,2-dibromoethane in DMF in the presence of potassium carbonate. Compounds **3**–**6** were isolated as single geometric isomers, which were identified as the *Z* isomers basing on the chemical shifts of the vinylic protons in the ^{1}H NMR spectra [28]. The preferential generation of *Z* isomers for these compounds may be the result of the formation of an intramolecular hydrogen bond between the pyridine nitrogen atom and the N–H fragment of the thiohydantoin cycle. The *Z* configuration of ligands **3** and **6** in their coordination compounds was also confirmed by X-ray diffraction data for complexes **7** and **9** (see below).



Scheme 1. Synthesis of ligands **3**–**6**.

The hydantion complexes **7**–**9** were obtained under the slow diffusion of diethyl ether into a mixture of methanolic solutions of the ligand **3**, **5** or **6** and copper(II) chloride dihydrate. All the isolated coordination compounds contain deprotonated hydantoin ligands in their structures (Scheme 2).

All the complexes were characterized by IR spectroscopy and elemental analysis; the structures of complexes **7** and **9** were also confirmed by X-ray diffraction data.

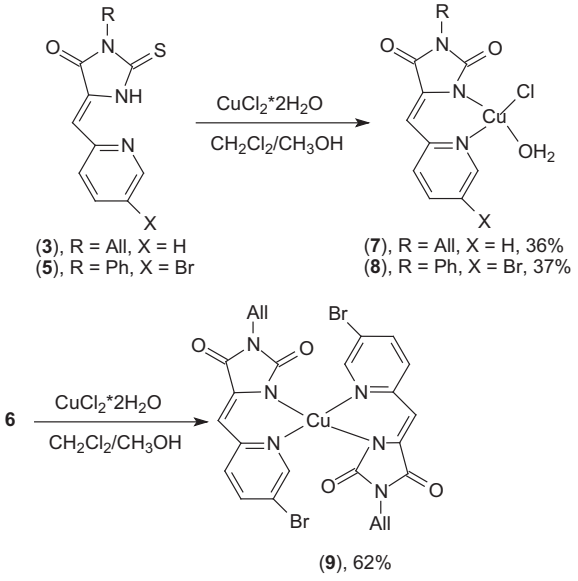
The IR spectra of complexes **7** and **8** show shifts in the absorption bands for the C=O, C=N and C=C groups from 1730 to 1630 cm^{-1} to lower frequencies relative to those of the initial ligands, whereas for complex **9** there is a shift of these absorption bands to higher frequencies as compared to the corresponding ligand **6**. The bathochromic shift of the C=O and C=N group bands in the IR spectrum of compound **9** compared to the bis-imidazolone **6** may be explained by the inclusion of a carbonyl group of the latter compound in the cross-π-conjugated bonds system, and the absence of such a cross-coupling in the first case. The lack of absorption of N(3)–H in the copper complexes suggests that the copper atom is bound to the hydantoin ligand at the N(3) position.

Single crystal data for complexes 7 and 9 were collected on SMART APEX II (Mo Kα) and CAD4 (Cu Kα) diffractometers, respectively. Crystallographic data and refinement parameters for **7** and **9** are presented in Table 1S in the Supporting information, and selected bond lengths are given in Table 1. The molecular structures of compounds **7** and **9** are shown in Figs. 1 and 2, respectively. Both compounds **7** and **9** have similar structures. DIAMOND drawings of each complex show that the pyridyl and imidazole rings of the organic ligands are nearly coplanar. For both complexes **7** and **9** the ligands are coordinated to the metal atom through their nitrogen atoms with the formation of six-membered metallacycles. The allyl fragment C_3H_5 is attached to the N(3) atom of the imidazole ring in a mutually perpendicular fashion.

The first difference between the structures of complexes **7** and **9** is the presence of a bromine atom in the pyridine ring in the *meta*-position for compound **9**, but this does not have a significant influence on the organic ligand structure: the differences in the corresponding bond lengths of the ligand moieties for **7** and **9** mainly do not exceed 0.01 Å, with a maximal distinction of 0.03 Å.

The coordination polyhedra of the copper atoms in the structures of the coordination compounds are significantly different. The copper atom in complex **7** is five-coordinated and the coordination polyhedra may be described as a square pyramid with an elongated apical Cu–Cl distance (2.6572(9) Å), which is common for such complexes [27]. In contrast, in complex **9** four nitrogen atoms from two ligand moieties form a coordination polyhedron around the copper atom which can be described as either a strongly distorted tetrahedron or a deformed square. The later description may be assumed to be preferred because of the steric effect of the two large ligands: their planes are inclined at 58.65° relative to each other.

An essential difference between structures **7** and **9** is also their molecular packing. The crystal structure of **9** is stabilized by stacking of pyridylmethylene-imidazolone fragments (the interplanar distance between parallel ligands moieties from neighboring molecules is about 3.5 Å; see Fig. 1S, Supporting information). At the



Scheme 2. Syntheses of copper hydantoin complexes **7**–**9**.

Table 1
Relevant interatomic distances for compounds **7** and **9**.

Compound **7**		Compound **9**	
Atoms	Distance (Å)	Atoms	Distance (Å)
Cu1–N1	2.044(3)	Cu1–N1	2.019(2)
Cu1–N2	1.982(3)	Cu1–N2	1.904(3)
Cu1–Cl1	2.3176(9)		
Cu1–Cl1′	2.6572(9)		
Cu1–O3	1.978(2)		
C6–C7	1.346(4)	C6–C7	1.342(4)
C6–C1	1.439(5)	C7–C8	1.434(4)
Imidazole ring, ranges			
C–N	1.366–1.399	C–N	1.368–1.406
C–C	1.492	C–C	1.507
C–O	1.221–1.235	C–O	1.209–1.213
Pyridine ring, ranges			
C–N	1.361–1.363	C–N	1.342–1.361
C–C	1.374–1.399	C–C	1.353–1.417
Allyl group			
N3–C10	1.459(4)	N3–C11	1.461(5)
C10–C11	1.501(5)	C11–C12	1.473(6)
C11–C12	1.297(5)	C12–C13	1.299(7)

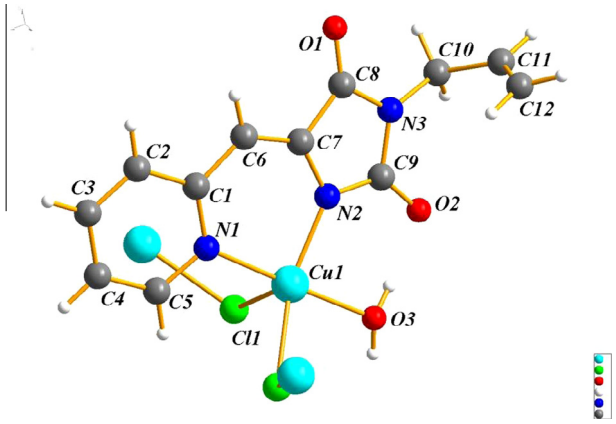


Fig. 1. Molecular structure and labelling scheme for complex **7**. The copper atoms are connected in chains via chlorine atoms.

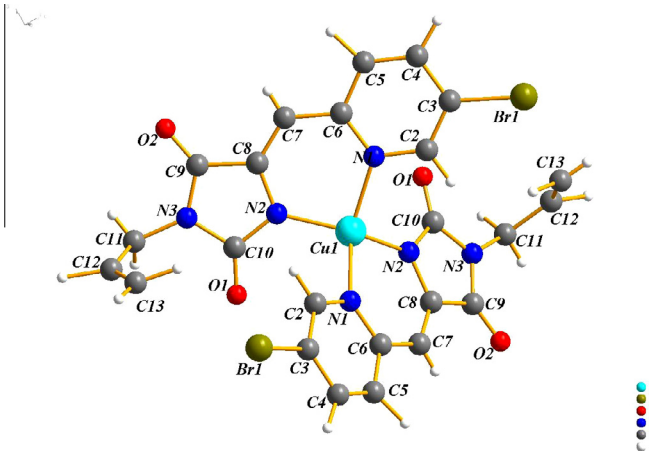


Fig. 2. Molecular structure and labelling scheme for complex **9**.

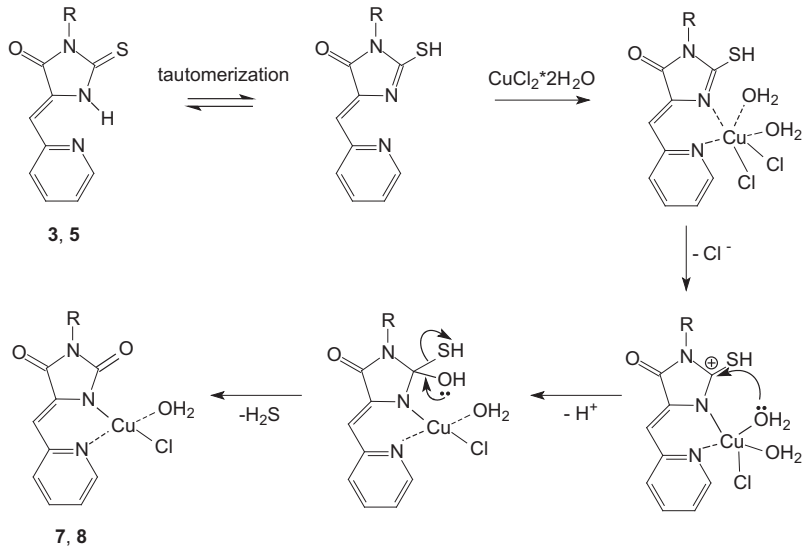
same time, compound **7** may be considered as 1D structure with (–Cl–Cu–Cl–) zigzag chains propagating along the *a* direction of the unit cell. The imidazole ligands are perpendicular to the chains and are parallel to each other, being about 3.7 Å apart.

The hydantoin-containing complexes **7**–**9** apparently form as a result of copper ion-mediated (as a Lewis acid) nucleophilic substitution of a ligand sulfur atom by a water molecule from $CuCl_2 2H_2O$ (Scheme 3). In the cases of the thiohydantoins **3** and **5**, the reaction apparently involved the iminothiol containing tautomeric form of the parent compounds. It appears that in the first stage of the complexation reaction the copper(II) ion is coordinated to the pyridine and thiohydantoin nitrogen atoms, which increases the electrophilic reactivity of bonding with the N(3) sp^2 hybridized carbon atom. Then, after the consecutive chloride elimination, water molecule attack on the C(2) atom, proton elimination and cleavage of the C–S bond, the hydantoin-containing copper(II) coordination compound forms. The liberated hydrogen sulfide or 1,2-ethanedithiol may bind to other copper ions, with the corresponding sulfide or thiolate formation, which explains the fact that the yields of the hydantoin complexes **7** and **8** do not exceed 50%.

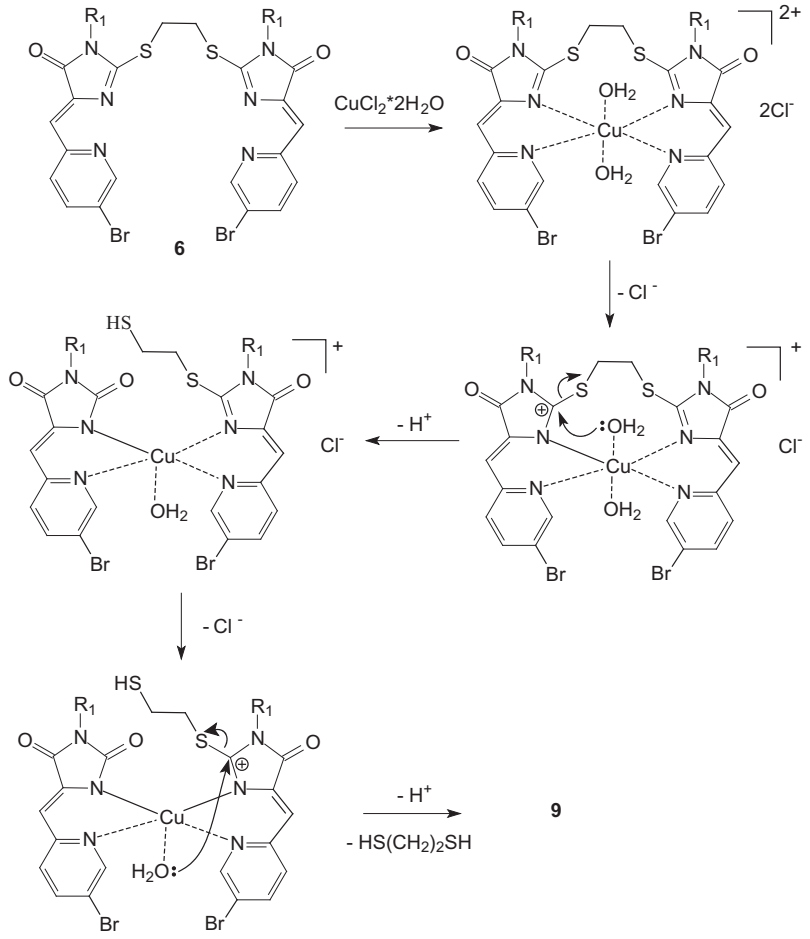
In the course of complex **9** formation, a coordination compound, wherein the starting bis-pyridyl-imidazolon **6** acts as a tetradentate ligand, apparently forms in the first stage, as analogously described in [26d]. Then the reaction proceeds via a mechanism similar to the formation of complexes **7** and **8**, with the sequential replacement of two sulfur-containing fragments and the formation of the bis-hydantoin complex (Scheme 4).

The assumption about the initial formation of a copper complex with pyridylmethylene-substituted 2-thio-imidazolone is confirmed by the number of hydantoin fragments in the complexes formed from the bis-thio-imidazolone ligand **6** and mono-thio-imidazolone ligands **3** and **5**. In the first case, a complex having two coordinating pyridylmethylene-2-thio-imidazolone moieties around the metal ion should be formed in the initial stage of the ligand interaction with $CuCl_2 2H_2O$. In accordance with this preorganization, complex **9** also contains two hydantoin moieties in the copper coordination sphere. In contrast, the interaction of the mono-pyridylmethylene-2-thio-imidazolone ligands **4** and **5** with Cu(II) leads to the formation of complexes containing a single thiohydantoin ligand and this results in the mono-hydantoin complexes **7** and **8**.

An alternative mechanism involving a ring opening-ring closure sequence, which have been proposed for thiohydantoin hydrolysis in alkaline medium [15], is unlikely in the absence of a sufficiently strong nucleophile. Note, that anhydrous copper(II) chloride does not form crystalline products under reaction with ligands **3**–**6** under the same conditions.



Scheme 3. A possible mechanism of hydantoin moiety formation during the preparation of complexes **7** and **8**.



Scheme 4. A possible mechanism for complex **9** formation.

4. Conclusion

The present study involves the synthesis of mono- and bis-hydantoin copper(II) complexes, obtained from the interaction of 5-pyridylmethylene-substituted 2-thiohydantoins or 2-alkylthio-3,5-dihydro-4H-imidazole-4-ones with $CuCl_2 2H_2O$. This finding demonstrates that the transformation of 2-thiosubstituted dihydro- and tetrahydro-imidazol-4-ones to the corresponding hydantoins can be initiated by the action of copper-containing Lewis acids. The information obtained in this study would be useful for understanding the mechanism of the interaction of copper compounds with sulfur-containing substances in biological systems.

Acknowledgements

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Appendix A. Supplementary data

CCDC 970870 and 970869 contain the supplementary crystallographic data for **7** and **9**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.03.045.

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