Synthesis, structure and electrochemistry of $Co^{II}LCl_2 \cdot 0.5MeCN$ {L = [2-(methylthio)-3-phenyl-5-(pyridin-2-ylmethylene)-3,5-dihydro-4*H*-imidazol-4-one]}

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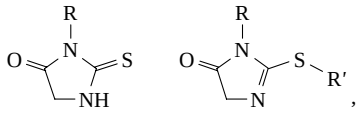
The reaction of 2-(methylthio)-3-phenyl-5-(pyridin-2-ylmethylene)-3,5-dihydro-4*H*-imidazol-4-one (L) with $CoCl_2 \cdot 6H_2O$ in $MeCN–CH_2Cl_2$ results in formation of the complex $CoLCl_2 \cdot 0.5MeCN$, which was characterised by single-crystal X-ray diffraction analysis and an electrochemical study.

In the last few years, considerable attention has been paid to the molecular systems containing 2-thiohydantoin units. Heterocyclic compounds of this type are attractive ligands because they can coordinate metal ions *via* nitrogen and/or sulfur donor atoms.[1–3] They can also form supramolecular networks by N–H···S and N–H···O hydrogen bonds.[4] Some 2-thiohydantions exhibit a wide range of pharmacological activities (anticonvulsant, antibacterial, antiviral and platelet aggregation inhibitory activities).[5–8]

Heterocyclic compounds such as 2-thiohydantoins and their alkylated analogues



which possess different endo- and exocyclic electron-donating atoms, are interesting chelating ligands towards metal ions.[1–3,9] Furthermore, the methylene carbon in the 5-position of these compounds is nucleophilic,[2] facilitating the synthesis of 5-substituted derivatives, with or without additional donor atoms. In particular, N-3 unsubstituted 5-(pyridin-2-yl-methylene)hydantoin in the reaction with $CuCl_2$ forms a supramolecular complex, in which the chelation of Cu^{II} ions by two nitrogen atoms is accompanied by the fastening of the organic fragments by hydrogen bonds.[9]

We studied the reactivity of 2-(methylthio)-3-phenyl-5-(pyridin-2-ylmethylene)-3,5-dihydro-4*H*-imidazol-4-one **1**,† which was obtained from 3-phenyl-2-thiohydantoin and 2-pyridine carboxaldehyde, towards cobalt(II) chloride. The reaction results in $Co^{II}LCl_2 \cdot 0.5MeCN$ adduct **2** (L = compound **1**).‡

As shown in Scheme 1, compound **1** has four potential donor atoms: the oxygen atom of the carbonyl group, the sulfur atom and two imine nitrogen atoms. Complexation with transition metal ions would occur through the nitrogen and sulfur atoms.

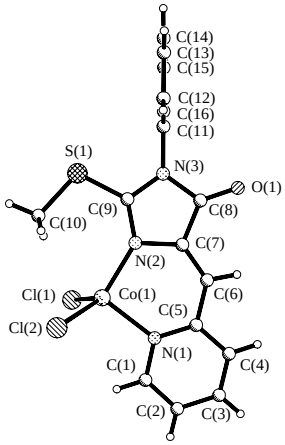
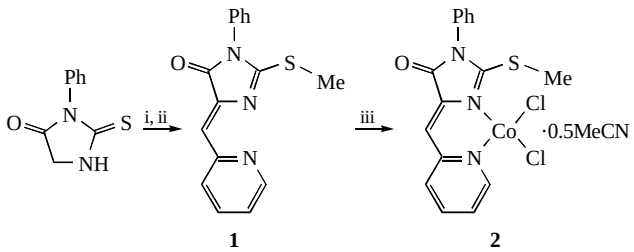


Figure 1 Molecular structure of **2** (only one of the two crystallographically independent molecules is shown). The important bond lengths (Å) and bond angles (°) (data for the second crystallographically independent molecule are given in parentheses): Co(1)–N(1) 2.044(3) [Co(1A)–N(1A) 2.028(6)], Co(1)–N(2) 1.992(5) [Co(1A)–N(2A) 2.022(3)], Co(1)–Cl(2) 2.2385(15) [Co(1A)–Cl(2A) 2.2466(15)], S(1)–C(9) 1.725(4) [S(1A)-C(9A) 1.711(7)], Co(1)–Cl(1) 2.267(2) [Co(1A)–Cl(1A) 2.2646(14)]; N(2)–Co(1)–N(1) 96.81(18) [N(2A)–Co(1A)–N(1A) 97.10(19)], N(2)–Co(1)–Cl(2) 120.18(14) [N(2A)–Co(1A)–Cl(2A) 114.53(12)], N(1)–Co(1)–Cl(2) 105.75(11) [N(1A)–Co(1A)–Cl(2A) 104.94(11)]; N(2)–Co(1)–Cl(1) 114.34(14) [N(2A)–Co(1A)–Cl(1A) 120.00(12)]; N(1)–Co(1)–Cl(1) 105.71(17) [N(1A)–Co(1A)–Cl(1A) 106.03(13)]; Cl(2)–Co(1)–Cl(1) 111.43(7) [Cl(2A)–Co(1A)–Cl(1A) 111.53(6)].

The molecular and crystal structures of **2** were determined by single-crystal X-ray diffraction analysis.§ The crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether vapour to a $MeCN–CH_2Cl_2$ (1:1) solution of the complex.

The molecular structure of complex **2** and the atom numbering are shown in Figure 1. The central cobalt atom is coordinated to two nitrogen atoms of the pyridine and thiohydantoin moieties and two chlorine atoms in a distorted tetrahedral fashion. The sulfur atom is staying away from coordination with cobalt (S–Co distances for both of the independent molecules are



Scheme 1 *Reagents and conditions*: i, 2-PyCHO, KOH, EtOH; ii, MeI, EtOH; iii, $CoCl_2 \cdot 6H_2O$, CH_2Cl_2, MeCN.

† 1 g (5.2 mmol) of 3-phenyl-2-thiohydantoin was dissolved in 14 ml of 2% KOH solution in ethanol with vigorous stirring. When the solution became clear, 0.56 g (5.2 mmol) of 2-pyridine carboxaldehyde was added by drops. The mixture was stirred for 12 h, after that 0.74 g (5.2 mmol) of methyl iodide was added to the mixture. The precipitate was filtered off and recrystallised from EtOH–DMF (3:1). The yield of 2-(methylthio)-3-phenyl-5-[(*Z*)-pyridin-2-ylmethylene]-3,5-dihydro-4*H*-imidazol-4-one was 67%. Mp 206 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 8.69 (d, 1H, $H_{\alpha'}$-Py, *J* 8.3 Hz), 8.53 (d, 1H, H_{β}-Py, *J* 4.4 Hz), 8.03 (t, 1H, H_{γ}-Py, *J* 4.4 Hz), 7.46 (m, 6H, H_{β}-Py, Ph), 6.88 (s, 1H, CH=), 2.70 (s, 3H, Me). ^{13}C NMR ([$^2H_6$]DMSO) δ: 173.5, 166.7, 165.2, 151.8, 147.9, 138.1, 134.1, 127.5, 127.2, 125.2, 122.1, 121.1, 11.3. IR (KBr, ν/cm^{-1}): 1730 (C=O), 1650 (C=N), 1600 (C=C). Found (%): C, 64.77; H, 4.54; N, 14.25. Calc. for $C_{16}H_{13}OSN_3$ (%): C, 65.08; H, 4.41; N, 14.24.

‡ 3 ml of acetonitrile was added to a solution of 10 mg (0.034 mmol) of 2-(methylthio)-3-phenyl-5-[(*Z*)-pyridin-2-ylmethylene]-3,5-dihydro-4*H*-imidazol-4-one in 2–3 ml of methylene chloride to give two phases. After that the solution of 8 mg (0.034 mmol) of $CoCl_2 \cdot 6H_2O$ in 3 ml of acetonitrile was slowly added. Crystals suitable for X-ray analysis were obtained from the solution after diethyl ether diffusion. Yield of **2** 82%. IR (KBr, ν/cm^{-1}): 1756, 1746 (C=O), 1644 (C=N), 1594 (C=C).

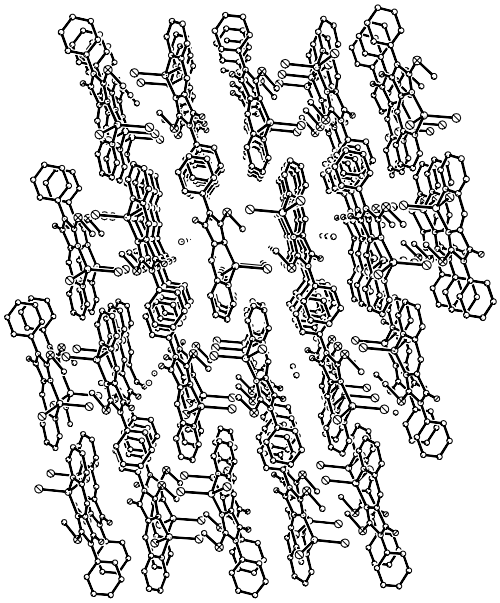


Figure 2 Crystal structure of **2** viewed down the crystallographic *a* axis. The hydrogen atoms are omitted for clarity.

3.896–3.897 Å), and the methyl group bound to sulfur is closer to the coordinated cobalt centre.

The molecules of organic ligands in the complex structure are not planar, since phenyl rings at N(3) and five-membered rings are tilted in respect to each other (the dihedral angles between the corresponding planes are 88.6° and 89.3° for two independent molecules). Thiohydantoin and pyridine rings are practically coplanar.

The nearest intermolecular contacts found in the structure of **2** are the contacts between the chlorine atom and one of the hydrogen atoms of the methyl group of the adjacent centrosymmetric molecule (2.903 Å). This interaction results in dimers associated by CH–Cl-type hydrogen bonds (the sum of the van der Waals radii of hydrogen and chlorine atoms is 3.01 Å[10]). Moreover, the carbon atoms of methyl groups are at a distance of 3.332 Å, and this distance is also shorter than the sum of the van der Waals radii of carbon (3.70 Å[10]). The above dimers form a layered crystal structure, in which the layers of type A dimers alternate with the layers of type B dimers (Figure 2).

The π–π interactions of aromatic rings in the crystal structure of **2** are not found. The nearest distance between the centroids of benzene rings (4.553 Å) is the distance between the benzene rings of the adjacent independent molecules. This distance does not fall into the range of those typical of π–π interactions.[11] However, it is worth noting that the adjacent crystallographically independent layers are linked by the week interaction of the 'CH-aromatic ring' type because the shortest distance between the carbon atoms of adjacent crystallographically independent molecules [C(15) and C(16A) atoms] is 3.374 Å.[11]

In the crystal structure of **2**, there is one additional acetonitrile molecule per two crystallographically independent complex molecules. Acetonitrile molecules occupy the voids between the stacks of dimers A and B (Figure 2).

The electrochemistry of free ligand **1** and complex **2** was studied by cyclic voltammetry (CV) in dry MeCN in the presence of 0.05 M Bu_4NBF_4 as an indifferent electrolyte. The results of redox potential measurements for **1**, **2** and $CoCl_2 \cdot 6H_2O$ are given in Table 1.

Table 1 Electrochemical oxidation (E^{Ox}) and reduction (E^{Red}) potentials [*vs.* Ag/AgCl/KCl(saturated)] of **1**, **2** and $CoCl_2 \cdot 6H_2O$ (concentration 10^{-3} mol dm^{-3}). Carbon glassy electrode, MeCN, 0.05 M Bu_4NBF_4.

Compound	$-E^{Red}$/V	E^{Ox}/V	Notes
1	1.29 1.77 1.99	1.71 2.16	Using a Pt working electrode, oxidation peaks appear at 1.69 and 2.25 V; at an Au electrode, at 1.65 and 2.20 V.
2	0.58 1.30 1.67 1.99	1.82 2.10	At Pt or Au electrodes, the first oxidation peak shifts to 1.52 V (Pt) or 1.29 V (Au); the second oxidation peak is not observed.
$CoCl_2 \cdot 6H_2O$	0.84[a] 1.12[b]	1.56 1.72	[a]On thoroughly cleaning the electrode surface. At the second potential scan, the first reduction peak decreases and, beginning with the third scan only, one wave is observed at –1.32 V. [b]When the potential is scanned into anodic site after reaching E = –1.12 V, the peak of the oxidative desorption of Co metal can be observed at +0.24 V.

For free ligand **1**, the CV curve shows three reduction peaks and two oxidation peaks (Figure 3). For complex **2**, four peaks can be observed in the cathodic region, from which the first (–0.58 V) probably results from the reduction of Co^{II}, and the potentials of the following peaks are close to the potentials of three cathodic peaks of the free ligand. We believe that complex **2** does not dissociate significantly into free ligand **1** and $CoCl_2$ during the electrochemical experiments. This was proved by the comparison of CV curves of the complex, the free ligand and $CoCl_2 \cdot 6H_2O$, which showed essential differences in their electrochemical behaviours (Figure 3, Table 1).

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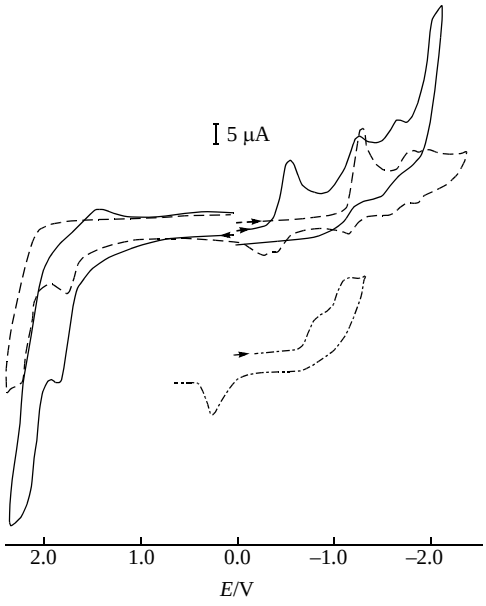

Figure 3 Cyclic voltammograms of **1** (dashed line), **2** (solid line) and $CoCl_2 \cdot 6H_2O$ (dash-dot line) (MeCN, 0.05 M Bu_4NBF_4).

§ *Crystallographic data for* **2**: crystals of $C_{17}H_{14.5}N_{3.5}OSCl_2Co$ are dark green prisms, M = 445.71. Crystal size: 0.6×0.5×0.3 mm, monoclinic, space group $P2_1/n$; unit cell dimensions a = 8.848(4), b = 11.332(4), c = 21.332(8) Å; V = 1900.2(13) Å^3, Z = 4, d_{calc} = 1.558 g cm^{-3}. X-ray diffraction of **2** measured with a Syntex P21 diffractometer at 293 K [graphite monochromator, λ(MoKα) = 0.71073 Å, ω-scan with a step of 0.3°]. The structure was solved by a direct method (SHELXS-97) and refined by the full-matrix least-square technique against F^2 for all non-hydrogen atoms (SHELXL-97). F(000) = 904. Limiting indices: $0 \le h \le 11$, $-13 \le k \le 5$, $-27 \le l \le 26$; reflections collected/unique 4760/4530 [R(int) = 0.0191]; goodness-on-fit on F^2 0.977; R indices [for 3283 rfls with $I > 2\sigma(I)$]: R_1 = 0.0421, wR_2 = 0.0937; R indices (all data): R_1 = 0.0780, wR_2 = 0.1053. Largest diff. peak and hole, 0.306 and –0.324 eÅ^{-3}, respectively.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 238622. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2004.

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