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The first example of a reversibly reducible Co^{II} complex with an anionic 2-thiohydantoin-type ligand

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The reaction of the potassium salt of 3-phenyl-5(*Z*)-(pyridin-2-ylmethylene)-2-thioxoimidazolidin-4-one (KL) with $CoCl_2 \cdot 6H_2O$ in MeCN results in formation of the neutral complex Co^{II}L$_2$. According to single-crystal X-ray analysis, the Co^{II} centre is coordinated to four nitrogen atoms of two organic ligands and has a distorted tetrahedral geometry. This complex undergoes electrochemical reduction with consequent two reversible and one quasi-reversible stages.

A catalytical cycle of some Co-containing enzymes involves the stage of alkyl group transportation from a metal-alkylated form of enzyme containing a Co^{III}-R fragment to a substrate.[1] In these enzymes, the cobalt centre is usually coordinated to four donor atoms, which can be nitrogen or nitrogen and sulfur.[2–6] Functional like metal chelate complexes potentially would be used as catalysts for electrochemically activated alkylation reactions: their single- or two-electron reduction results in formation of reduced complexes, very active in S$_N$2 reactions with different alkylating agents.[7] In quest of model complexes for active centres

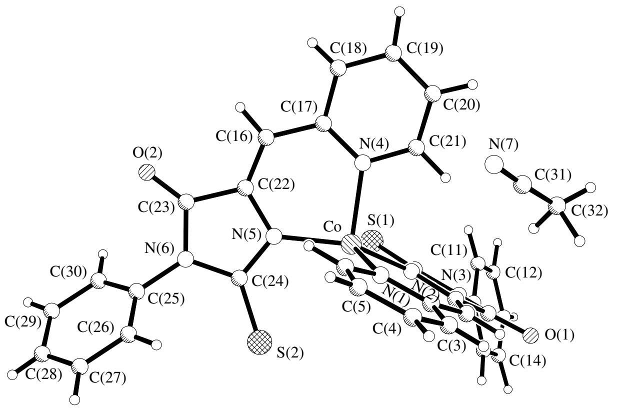
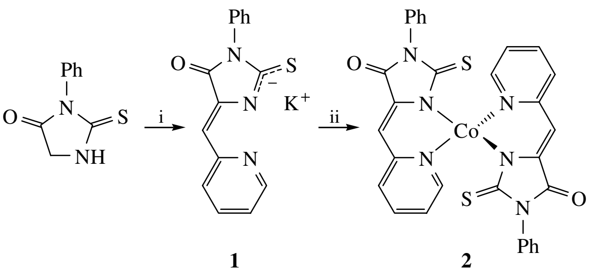


Figure 1 Molecular structure of **2**. The important bond lengths (Å) and bond angles (°): Co–N(1) 2.019(2), Co–N(2) 1.9162(19), Co–N(4) 2.031(2), Co–N(5) 1.904(2), S(1)–C(9) 1.711(7); N(5)–Co–N(2) 148.78(9), N(5)–Co–N(1) 108.39(9), N(2)–Co–N(1) 92.02(8), N(5)–Co–N(4) 91.60(8), N(2)–Co–N(4) 108.96(9), N(1)–Co–N(4) 98.38(9).

of Co-containing redox enzymes, we previously investigated the cobalt(II) complex of S-alkylated 5-pyridinemethylene-2-thiohydantoin.[8] 2-Thiohydantoins (2-thioxoimidazol-4-ones) and their S-alkylated derivatives are ligands, which can coordinate metal ions *via* nitrogen and/or sulfur donor atoms.[9–12] Complexes with uncharged N_2-type ligands are reduced irreversibly in an electrochemical cell, which makes them unsuitable as catalysts for electrochemically activated reactions.[8]

Here, we describe the synthesis and electrochemical investigation of a Co^{II} complex with a monoanionic ligand derived from 3-phenyl-5(*Z*)-(pyridin-2-ylmethylene)-2-thioxoimidazolidin-4-one (LH). We found that the above complex exhibits two-step reversible electrochemical reduction, clearly differentiating it from previously characterised thiohydantoin-type complexes.

Under treatment of 3-phenyl-2-thiohydantoin with 2-pyridine carboxaldehyde in the presence of potassium hydroxide, corresponding salt KL **1**[†] was obtained. Then, the reaction of **1** with $CoCl_2 \cdot 6H_2O$ in refluxing acetonitrile results in formation of neutral complex **2**.[‡]



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

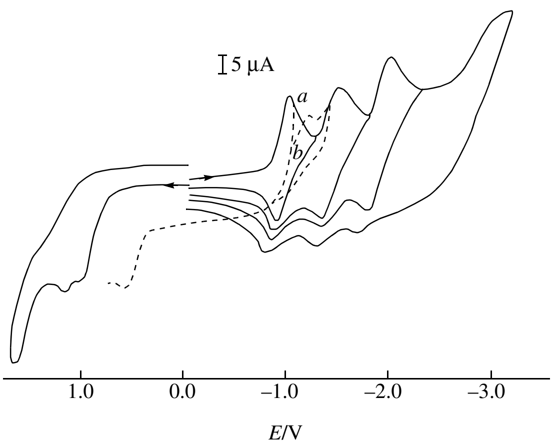


Figure 2 Cyclic voltammograms of **2** in free DMF (solid line) and after Bu^nI addition into the solution (dash line) (DMF, 0.05 M Bu_4NClO_4). The vertical distance [*a*,*b*] corresponds to a reduction of the current value on a suspension of potential scanning for 15 s. Further scanning of the potential to the cathode region reveals a new peak at –1.20 V; in addition, the oxidation peak of I^- appears on the reoxidation curve at +0.56 V.

The molecular and crystal structure of **2** was determined by single-crystal X-ray diffraction analysis.[§] According to this analysis, the crystals of the product have the composition L_2Co MeCN. The molecular structure of complex **2** together with the atom numbering scheme and the selected geometric parameters is shown in Figure 1. The coordination geometry of the cobalt(II) atom represents a distorted tetrahedron. The metal atom is surrounded by four nitrogen atoms from two distinct ligand molecules, which utilize their pyridine nitrogen atoms and thiohydantoin N(1) nitrogen atoms for coordination. In a crystal, the shortest intermolecular interaction between complex molecules is S(2)···H(4) [2.773(5) Å; 1 – *x*, 0.5 + *y*, 0.5 – z].

The electrochemistry of complex **2** was investigated using cyclic voltammetry (CV) in dry DMF in the presence of 0.05 M Bu_4NClO_4 as an indifferent electrolyte.

For complex **2**, four peaks were observed in the cathodic region, from which the first ($E_{1/2}$ –0.92 V) and the second ($E_{1/2}$ –1.34 V) correspond to reversible single-electron reduction steps. The third single-electron wave ($E_{1/2}$ –1.80 V) is quasi-reversible, while the fourth wave (E_p –2.06 V) is irreversible. In the anodic region, a CV curve shows two irreversible waves with E_p 0.76 and 1.26 V (Figure 2, solid line). The observed electrochemical reversibility of the first reduction wave shows that the reduced anionic complex (containing either Co^I, if the reduction is localised on the Co centre, or the reduced radical anion form of the ligand) is a rather stable particle in the solution. Therefore, it may be expected that the complex will be alkylated at the Co atom (or at the ligand).[13]

[†] 2 g (0.01 mol) of 3-phenyl-2-thiohydantoin was dissolved in 15 ml of a 2% ethanolic solution of KOH with vigorous stirring. After the solution became clear, 0.60 g (0.01 mol) of 2-pyridine carboxaldehyde was added in drops, and the solution was stirred for 12 h. The precipitate was filtered off and washed with a small amount of water. Yield of the potassium salt of 3-phenyl-5-[(*Z*)-3-pyridinemethylidene]-2-thiohydantoin **1** was 85%. Mp 295 °C. ^{1}H NMR (400 MHz, [$^2H_6$]DMSO) δ: 8.82 (d, 1H, H_α-Py, *J* 4.7 Hz), 8.50 (d, 1H, H_β-Py, *J* 8.3 Hz), 7.77 (t, 1H, H_β-Py, *J* 7.9 Hz), 7.40 (m, 6H, H_γ-Py, H-Ph), 6.97 (s, 1H, =CH). IR (KBr, ν/cm^{-1}): 1730 (C=O), 1650 (C=N), 1600 (C=C). Found (%): C, 55.99; H, 3.25; N, 13.23. Calc. for $C_{15}H_{10}OSN_3K$ (%): C, 56.23; H, 3.46; N, 13.11.

[‡] 0.0003 mol of the potassium salt of 3-phenyl-5-[(*Z*)-3-pyridinemethylidene]-2-thiohydantoin **1** was dissolved in 20 ml of MeCN with heating. To this solution, 0.003 mol of cobalt(II) chloride hexahydrate was added. The reaction mixture was heated under reflux for 3 h and then cooled. The solvent was removed to a half of its volume. The crystals suitable for X-ray analysis were obtained. Mp 269 °C. Yield of **2**, 82%. IR (KBr, ν/cm^{-1}): 1756, 1746 (C=O), 1644 (C=N), 1594 (C=C).

[§] *Crystallographic data for* **2**: crystals of $C_{16}H_{11.50}Co_{0.50}N_{3.50}OS$ are dark green prisms, *M* = 330.31. Crystals (0.35×0.22×0.18 mm) are monoclinic, space group $P2_1/c$; *a* = 13.416(3), *b* = 16.593(3) and *c* = 15.095(3) Å; *V* = 3027.4(11) Å, *Z* = 4, d_{calc} = 1.449 g cm^{-3}. X-Ray diffraction of **2** measured with a Syntex $P2_1$ 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) = 1356. Limiting indices $-15 \le h \le 14$, $0 \le k \le 12$, $-0 \le l \le 17$. Reflections collected/unique 4370/4202 (R_{int} = 0.0328); GOF = 0.885 on F^2; *R* indices [for 3283 reflections with $I > 2\sigma(I)$]: R_1 = 0.0284, wR_2 = 0.0704; *R* indices (all data): R_1 = 0.0685, wR_2 = 0.0754. Largest diffraction peak and hole, 0.226 and –0.244 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 266636. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2005.

Indeed, when an alkylating agent (Bu^nI) was added to the solution (Figure 3, dash line), a new peak ($E_p = -1.20$ V) arised already at the first potential scanning; its height increased with the electrolysis time at potentials of the first peak of compound **2**. At the same time, the reversibility of the first peak disappears (its height strongly decreases), and in the anodic region a new peak arises ($E_p \sim 0.56$ V) at the potential scanning into anodic region, which corresponds to iodide ion oxidation. Such typical changes show that there is the electrochemically induced fast alkylation reaction of complex **2** in this system.[13]

In summary, we synthesised and structurally characterised a new Co^{II} complex with an anionic thiohydantoin-type ligand. This complex is of great interest for the following reasons: (1) this is a first Co^{II} complex with an anionic thiohydantoin ligand containing the additional coordinating donor group attached to the 5-position and (2) this compound is the first example of reversibly reducible thiohydantoin-cobalt complexes, which is potentially of interest because of its possible electrocatalytical activity in alkylation reactions.

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References

1 G. J. Gerfen, S. Licht, J. P. Willems, B. M. Hoffman and J. Stubbe, *J. Am. Chem. Soc.*, 1996, **118**, 8192.

2 C. D. Carr, J. M. Sirovatka and R. G. Finke, *J. Am. Chem. Soc.*, 1996, **118**, 11142.

3 C. D. Carr, J. M. Sirovatka and R. G. Finke, *Inorg. Chem.*, 1996, **35**, 5912.

4 B. A. Brennan, G. Alms, M. J. Nelson, L. T. Durney and R. C. Scarrow, *J. Am. Chem. Soc.*, 1996, **118**, 9194.

5 S. Dong, R. Padmakumar, R. Banerjee and T. G. Spiro, *J. Am. Chem. Soc.*, 1996, **118**, 9182.

6 K. L. Brown, S. Cheng, J. D. Zublowski and E. J. Valente, *Inorg. Chem.*, 1996, **35**, 3442.

7 R. D. Rakhimov, Yu. A. Vainstein, E. V. Lileeva, N. N. Zheligovskaya, M. Ya. Mel'nikov and K. P. Butin, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1089 (*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1150).

8 A. G. Majouga, E. K. Beloglazkina, S. Z. Vatsadze, A. A. Moiseeva, K. P. Butin and N. V. Zyk, *Mendeleev Commun.*, 2004, 115.

9 M. M. Chowdhry, A. Burrows, D. M. Mingos, A. J. White and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1995, 1521.

10 J. Casas, E. Castellano, A. Macfas, N. Playa, A. Sanchez, J. Sordo and J. Zukerman-Schpector, *Inorg. Chim. Acta*, 1995, **238**, 129.

11 M. Arca, F. Demartin, F. Davillanova, A. Garau, F. Isaia, V. Lippolis and G. Verani, *Inorg. Chem.*, 1998, **37**, 4164.

12 M. M. Chowdhry, D. M. Mingos, A. J. White and D. J. Williams, *Chem. Commun.*, 1996, 899.

13 E. K. Beloglazkina, A. A. Moiseeva, A. V. Churakov, I. S. Orlov, N. V. Zyk, J. A. K. Hovard and K. P. Butin, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 436 (*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 467).

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