

New coordination compounds of uranyl ion with 3-(2-hydroxyphenyl)-1,2,4-triazole and its derivatives: synthesis and investigation of spectral properties

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New methods of 3-(2-hydroxyphenyl)-1,2,4-triazoles synthesis were developed. Obtained ligands was used for synthesis of three new complex compounds of uranyl-ion with general composition $[\text{UO}_2(\text{HL})_2(\text{Solv})]$. These compounds were characterized by NMR and IR spectroscopy.

Introduction

The synthesis and investigation of new coordination compounds of uranyl with organic ligands allows developing of new functional materials, such as sensors for alkali metals ions [1] or electrophilic addition reactions catalysts [2]. Hydrophobic ligands could be used as extractants which transfer uranyl ion to the organic phase [3-4]. New methods of spectrophotometric determination of trace amounts of uranium, which is very important to detect radioactive contamination, based on the use of organic ligands are also actively developing part of modern chemistry [5].

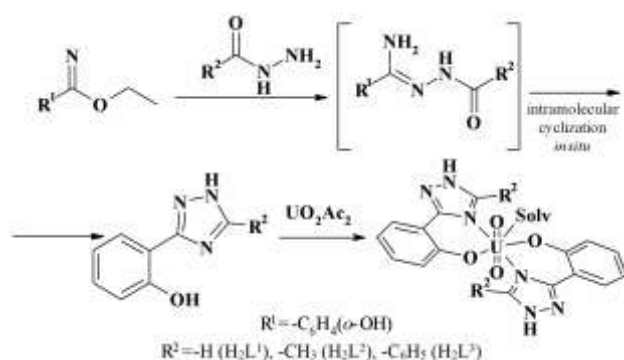
Well known that uranyl ion is a hard Lewis acid, so it is readily form coordination compounds with O-containing ligand systems. But there are also number of reports describing uranyl compounds with O,N-donor ligands [6-

7]. Depending on the desired properties of the complex as O-containing part usually acts carboxylic [6] or hydroxyphenyl group [2c, 7-8]. The most common N-containing fragments is azomethine group [2c, 7, 9]. Five or six-membered nitrogen containing heterocycles are also used [6a, 10].

Considerable attention among heterocycles attracting to 1,2,4-triazoles. Previously we report synthesis of mononuclear complexes with 5-(2-hydroxyphenyl)-1,2,4-triazolylacetic acid [11], 3-(2-hydroxyphenyl)-5-(2-pyridyl)-1,2,4-triazole [12] and 3,5-(2-hydroxyphenyl)-1,2,4-triazole [13]. In all cases ligands showed tridentate coordination mode. In this paper we focused on synthesis of uranyl complexes with 3-(2-hydroxyphenyl)-1,2,4-triazole and its derivatives which act as bidentate ligands.

Results and discussion

Ligands were obtained from corresponding carboxylic acids hydrazides and iminoesters (**Scheme 1**). This is a fairly common method of synthesis of triazole heterocycle [11-14]. Compared to other described methods it allows using simple and cheap starting materials [15]. Acylamidrazone which is formed by acylation of hydrazide with iminoester undergo intermolecular cyclization into triazole *in situ*.



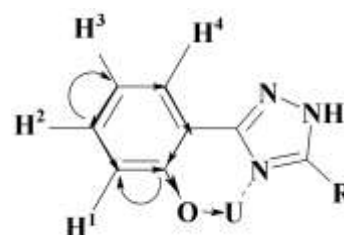
Scheme 1. Synthesis of 3-(2-hydroxyphenyl)-1,2,4-triazoles and $\text{UO}_2(\text{HL})_2(\text{Solv})$.

Obtained ligands easily form coordination compounds with uranyl ion. The disappearance of the signal of hydroxyl proton in the NMR spectra of the complex allows us to assume that in the process of complex formation deprotonation of hydroxyl groups take place. It results in neutral complexes formation. Absences of signals of acetates also prove formation of intramolecular coordination compounds.

For obtained complexes we propose structure depicted on **Scheme 1**, where ligands

together with molecule of solvent occupy equatorial positions of uranyl ion.

In the NMR spectrum of $[\text{UO}_2(\text{H}_2\text{L}^1)_2(\text{CH}_3\text{OH})]$ we observe high field shift of signals of protons H^1 , H^2 and H^4 , compared to the initial ligand spectra, caused to transmission of charge to uranium through a chain of atoms (**Scheme 2**). Low-field shift of signal of H^3 caused to mesomeric transition of charge from deprotonated hydroxyphenyl group.



Scheme 2. The distribution of the electron density in the aromatic system of $\text{UO}_2(\text{HL})_2(\text{Solv})$.

The stability of obtained complexes in solution depends on the substituent in 5-position of triazole heterocycle (**Figure 1**).

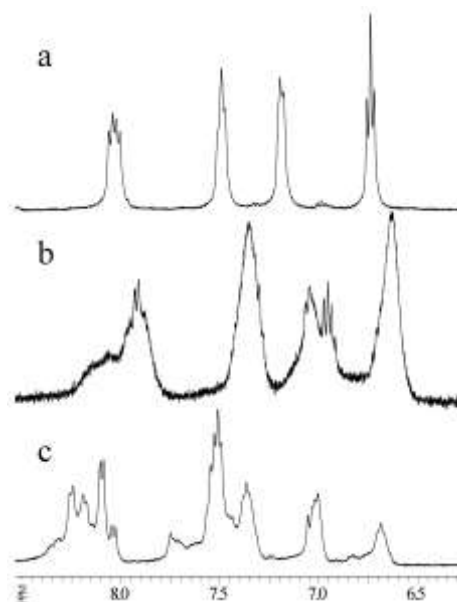


Figure 1. The signals of aromatic protons of complexes $[\text{UO}_2(\text{H}_2\text{L}^1)_2(\text{CH}_3\text{OH})]$ (a), $[\text{UO}_2(\text{H}_2\text{L}^2)_2(\text{H}_2\text{O})]$ (b) and $[\text{UO}_2(\text{H}_2\text{L}^3)_2(\text{CH}_3\text{OH})]$ (c).

In the case of $[\text{UO}_2(\text{H}_2\text{L}^1)_2(\text{CH}_3\text{OH})]$ there are sharp signals of complexes observed in spectra (**Figure 1a**). It means that $[\text{UO}_2(\text{H}_2\text{L}^1)_2(\text{CH}_3\text{OH})]$ do not dissociate in solution of DMSO. The signals in spectra of $[\text{UO}_2(\text{H}_2\text{L}^2)_2(\text{H}_2\text{O})]$ are broad (**Figure 1b**) and in the case of $[\text{UO}_2(\text{H}_2\text{L}^3)_2(\text{CH}_3\text{OH})]$ we observe also the signals of non-coordination ligands (**Figure 1c**). This allows us to assume that complexes **2** and **3** are partially dissociated in solution of DMSO and dissociations rate rise together with increasing of substituent volume. Also **2** and **3** can have high kinetic lability compared with **1** that is associated with dissociation of solvent molecules, which can explore broadening of proton signals in NMR spectra.

Conclusions

We have developed new methods of synthesis of 3-(2-hydroxyphenyl)-1,2,4-triazoles and received three new coordination compounds of uranyl ion. Obtained ligands form complexes with uranyl-ion to ligand molar ratio M:L = 1:2. Two complexes partially dissociate in DMSO solution, what was confirmed by ^1H NMR spectroscopy.

Experimental part

General

All used solvents and reagents are commercially available and were used without prior purification. Formylhydrazide, hydrazides

2-hydroxybenzoic and benzoic acids, imidoesters 2-hydroxybenzoic and acetic acid were obtained by the previously described methods [16-18]. ^1H NMR spectra were recorded in DMSO- d_6 solutions on a Varian Mercury 400 instrument. ^1H chemical shifts (δ) are given in ppm with positive values to high frequency relative to the tetramethylsilane resonances determined from the residual solvent peaks. IR spectra were recorded on a Spektrum BX Perkin Elmer.

Synthesis and characterizations

3-(2-hydroxyphenyl)-5-H-1,2,4-triazole (H_2L^1). To a solution of 20.0 g (0.107 mol) of 2-hydroxybenzoic acid ethyl iminoester hydrochloride in 250 ml of methanol 16.5 ml (0.117 mol) of triethylamine and 6.36 g (0,107 mol) formilhydrazide was added and refluxed for 3 hours. The reaction mixture was evaporated and diluted with wather. Solid residue was filtered, dried and recrystallized from 100 ml of toluene. Yield: 14.5 g, 84%. M.p. = 144-146 °C. ^1H NMR (DMSO- d_6 , 400 MHz): δ , m.p. (J, Hz): 14.41 (1H, s., NH); 11.33 (1H, s., OH); 8.53 (1H, s., CH); 7.97 (1H, d., $^3J_{\text{HH}} = 8$, o-PhOx, $^3J_{\text{HH}} = 7$); 6.94 (1H, t., $^3J_{\text{HH}} = 7$, m-PhOx); 7.32 (1H, t., $^3J_{\text{HH}} = 7$, p-PhOx); 6.99 (1H, d., $^3J_{\text{HH}} = 7$, m'-PhOx). IR(KBr, cm^{-1}): 3311, 3178-2411, 1614, 1595, 1546, 1490, 1445, 1387, 1359, 1284, 1263, 1266, 1219, 1201, 1162, 1130, 1108, 1085, 985, 887, 835, 739, 705. Anal. calc. for $\text{C}_8\text{H}_7\text{N}_3\text{O}$, %: C 59.62,

H 4.38, N 26.07. Found: C 59.58, H 4.34, N 26.09.

3-(2-hydroxyphenyl)-5-methyl-1,2,4-triazole

(H_2L^2). To a solution of 1.47 g (0.0171 mol) of acetic acid ethyl iminoester in 100 ml of methanol 2.0 g (0.0132 mol) 2-hydroxybenzhydrazide was added and refluxed for 6 hours. The reaction mixture was evaporated and residue was recrystallized from 50 ml of water. Yield: 0.7 g, 31%. M.p. = 166-167 °C. 1H NMR (DMSO- d_6 , 400 MHz): δ , m.p. (J, Hz): 14.09 (1H, s., NH); 11.26 (1H, s., OH); 2.47 (3H, s., CH₃); 7.94 (1H, d., $^3J_{HH} = 7$, o-PhOx); 6.95 (1H, t., $^3J_{HH} = 4$, $^3J_{HH} = 8$, m-PhOx); 7.27 (1H, t., $^3J_{HH} = 6$, p-PhOx); 7.94 (1H, d., $^3J_{HH} = 7$, m'-PhOx). IR (KBr, cm^{-1}): 3208, 3148, 3030, 2919, 2758, 2689, 1626, 1589, 1574, 1493, 1460, 1378, 1288, 1230, 1209, 1555, 1058, 892, 830, 747, 717, 674. Anal. calc. for C₉H₉N₃O, %: C 61.70, H 5.18, N 23.99. Found: C 61.74, H 5.19, N 23.96.

3-(2-hydroxyphenyl)-5-phenyl-1,2,4-triazole

(H_2L^3). To a solution of 6.49 g (0.035 mol) benzoic acid ethyl imidoester hydrochloride in 100 ml of methanol was added 4.92 ml (0,035 mol) triethylamine and 4.76 g (0,035 mol) 2-hydroxybenzhydrazide was added and refluxed for 40 hours. Result white precipitate was filtered and dried. Yield: 6.9 g, 88%. M.p. > 200 °C. 1H NMR (DMSO- d_6 , 400 MHz): δ , m.p. (J, Hz): 14.44 (1H, s., NH); 11.37 (1H, s., OH); 7.55 (1H, t., $^3J_{HH} = 8$, m-Ph); 7.53 (1H, t., $^3J_{HH} = 8$, p-Ph); 8.09 (1H, d., $^3J_{HH} = 8$, o-Ph); 7.04 (1H,

t., $^3J_{HH} = 8$, m-PhOx); 7.37 (1H, t., $^3J_{HH} = 8$, p-PhOx); 8.03 (1H, d., $^3J_{HH} = 8$, m'-PhOx); 7.00 (1H, d., $^3J_{HH} = 3$, o-PhOx). IR(KBr, cm^{-1}): 3238, 1629, 1589, 1529, 1493, 1463, 1435, 1372, 1306, 1248, 1140, 786, 754. Anal. calc. for C₁₄H₁₁N₃O, %: C 70.87, H 4.67, N 17.71. Found: C 70.86, H 4.71, N 17.75.

[UO₂(H₂L¹)₂(CH₃OH)] (1). To a 5 ml solution of 106.0 mg (0.25 mmol) UO₂(CH₃COO)₂·2H₂O in methanol was added 5 ml solution 88.5 mg (0.55 mmol) H₂L¹ in methanol. At slow crystallization [UO₂(H₂L¹)₂(CH₃OH)] for two days at room temperature from solution was fallen red crystals, which are filtered, washed with methanol (5 ml) and dried in air. Yield: 37%. 1H NMR (DMSO- d_6 , 400 MHz): δ , m.p. (J, Hz): 14.95 (2H, s., NH); 9.65 (1H, s., CH); 9.22 (1H, s., CH); 7.18 (1H, d., $^3J_{HH} = 8$, o-PhOx); 7.49 (1H, t., $^3J_{HH} = 8$, m-PhOx); 6.74 (1H, t., $^3J_{HH} = 8$, p-PhOx); 8.03 (1H, d., $^3J_{HH} = 8$, m'-PhOx); 3.17 (3H, s., CH₃OH). IR(KBr, cm^{-1}): 3130, 1608, 1582, 1496, 1457, 1296, 1257, 1127, 1092, 979, 892, 846, 756, 714, 590. Anal. calc. for C₁₇H₁₇N₆O₅U, %: C 32.75, H 2.75, N 13.48. Found: C 32.74, H 2.69, N 13.42.

[UO₂(H₂L²)₂(H₂O)] (2). To a 5 ml solution 106.0 mg (0.25 mmol) UO₂(CH₃COO)₂·2H₂O in water was added 5 ml solution 105.9 mg (0.625 mmol) H₂L² in acetonitrile. At slow crystallization [UO₂(HL²)₂(H₂O)] for two days at room temperature from solution was fallen dark red

crystals, which are filtered, washed with acetonitrile (5 ml) and dried in air. Yield: 39%. ¹H NMR (DMSO-d₆, 400 MHz): δ, m.p. (J, Hz): 14.60 (2H, s., NH); 2.72 (6H, s., CH₃); 6.53-8.23 (8H, PhOx). IR(KBr, cm⁻¹): 3327, 1604, 1579, 1489, 1459, 1308, 1263, 1136, 1036, 864, 750, 602. Anal. calc. for C₁₈H₁₉N₆O₅U, %: C 33.92, H 3.00, N 13.18. Found: C 33.88, H 3.04, N 13.15.

[UO₂(H₂L³)₂(CH₃OH)] (3). To a 5 ml solution of 106.0 mg (0.25 mmol) UO₂(CH₃COO)₂·2H₂O in methanol was added 5 ml solution 130.4 mg (0.55 mmol) H₂L² in methanol. At slow crystallization [UO₂(H₂L³)₂(CH₃OH)] for two days at room temperature from solution was fallen red crystals, which are filtered, washed with methanol (10 ml) and dried in air. Yield: 44%. ¹H NMR (DMSO-d₆, 400 MHz): δ, m.p. (J, Hz): 14.29 (2H, s., NH); 6.69-8.26 (18H, Ph, PhOx); 3.17 (3H, s., CH₃OH); 4.12 (1H, s., CH₃OH). IR(KBr, cm⁻¹): 3235, 1605, 1559, 1484, 1303, 1252, 1139, 889, 850, 735, 695, 605. Anal. calc. for C₂₉H₂₅N₆O₅U, %: C 44.91, H 3.2, N 10.84. Found: C 44.87, H 3.23, N 10.81.

References

[1] M. Cametti, L. Ilander, K. Rissanen, *Inorg. Chem.* **2009**, 48, 8632.
 [2] (a) H. Naeimi, A. Karshenas, *Polyhedron*. **2013**, 49, 234. (b) V. A. Castelli, A. D. Cort, L. Mandolini, D. N. Reinhoudt, L. Schiaffino, *Chem. Eur. J.* **2000**, 6(7), 1193. (c) A. D. Cort, L. Mandolini, L. Schiaffino, *J. Org. Chem.* **2008**, 73, 9439.

[3] Y. K. Agrawal, P. Shrivastav, S. K. Menon, *Separation/Purification Technology*. **2000**, 20, 177.
 [4] A. C. Sather, O. B. Berryman, J. Jr. Rebek, *Chemical Science*. **2013**, 4, 3601.
 [5] (a) J. Michon, S. Frelon, C. Garnier, F. Coppin, *J Fluoresc.* **2010**, 20, 581. (b) E. G. Santos, C. S. Tomiyama, C. A. Kodaira, A. V. S. Lourenço, M.C.F.C. Felinto, H. F. Brito, M. E. F. Brito, *INAC 2009*, Rio de Janeiro, RJ, Brazil.
 [6] P. M. Cantos, M. Frisch, C. L. Cahill, *Inorg. Chem. Com.* **2010**, 13, 1036.
 [7] (a) A. D. Cort, J. I. M. Murua, C. Pasquini, M. Pons, L. Schiaffino, *Chem. Eur. J.* **2004**, 10, 3301. (b) F. Y. Mihan, S. Bartocci, A. Credi, S. Silvi, A. D. Cort, *Supramolecular Chemistry*. **2013**, 25(2), 109.
 [8] L. A. Borkowski, C. L. Cahill, *Crystal Growth & Design*. **2006**, 6(10), 2241.
 [9] M. Shebl, S. M. E. Khalil, F. S. Al-Gohani, *Journal of Molecular Structure*. **2010**, 980, 78.
 [10] S. M. E. Khalil, *J. Coord. Chem.* **2003**, 56, 12, 15, 1013
 [11] (a) D. M. Khomenko, R. O. Doroschuk, O. V. Vashchenko, R. D. Lampeka, *Ukr. Khim. Zh.* **2014**, 80(12), 83.
 [12] I.V. Raspertova, R.O. Doroschuk; D.M. Khomenko, R.D. Lampeka, *Acta Crystallographica Section C: Crystal Structure Communications*, **2012**, 68(3), m61-m63.
 [13] D. M. Khomenko, R. O. Doroschuk, I. V. Raspertova, R. D. Lampeka, *Reports of the National Academy of Sciences of Ukraine*, **2012**, 7, 139 (in Ukrainian).
 [14] (a) A. S. Kiselyov, E. L. Piatnitski Chekler, N. B. Chernisheva, L. K. Salamandra, V. V. Semenov, *Tetrahedron Lett.* **2009**, 50, 3809. (b) D. Moderhack, J.-C. Schneider, *J. Heterocyclic Chem.* **2007**, 44, 393. (c) S.S. Woodard, K.D. Jerome, *Comb. Chem. High Throughput Screening*. **2011**, 14(2), 132.

[15] (a) D. Catarzi, L. Cecchi, V. Colotta, Filacchioni, C. Martini, L. Giusti, A. Lucacchini, G. Valle, *Farmaco*. **1994**, 49(2), 89. (b) E. Yu. Shasheva, N. I. Vikrishchuk, L. D. Popov, V. I. Minkin, M. E. Kletskii, M. Yu. Antipin, A. D. Vikrishchuk, I. E. Mikhailov, *Russian Journal of Organic Chemistry*. **2010**, 46(7), 1079. (c) G.N. Dorofeenko, et al. *Journal of Organic Chemistry USSR (English Translation)*, **1977**, 13, 2289.

[16] L.N. Volovel'skii, G.V. Knorozova, *J. Gen. Chem. USSR (Engl. Transl.)*, **1964**, 34(1), 343,341.

[17] *Organikum*. **1992**. M.: Mir, 2. 474 (in Russian).

[18] L.J. Darlage, T.H. Kinstle, C . L. McIntosh. *J. Org. Chem.*, **1971**, 56(8), 1088.