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[1]BENZOFURO[3,2-*c*]PYRIDINE
Synthesis and coordination reactions

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(*E*)-3-(1-Benzofuran-2-yl)propenoic acid (**1**) was prepared from 1-benzofuran-2-carbaldehyde under the Doebner's conditions. The obtained acid was converted to the corresponding azide **2**, which was cyclized by heating in diphenyl ether to [1]benzofuro[3,2-*c*]pyridine-1(2*H*)-one (**3**). This compound was aromatized with phosphorus oxychloride to chloroderivative **4** which was reduced with zinc and acetic acid to the title compound **5**. [1]Benzofuro[3,2-*c*]pyridine-2-oxide (**6**) was synthesized by reaction of **5** with 3-chloroperoxybenzoic acid in dichloromethane. Treatment of **6** with benzoyl chloride and potassium cyanide (Reissert–Henze reaction) was shown to produce the corresponding [1]benzofuro[3,2-*c*]pyridine-1-carbonitrile (**7**). The title compound was used for preparation of complexes $Cu_2(ac)_4(bfp)_2$ (**8**) and $CoCl_2(bfp)_2$ (**9**), where ac=$CH_3CO_2^-$ and bfp= [1]benzofuro[3,2-c]pyridine. Both oxygen atom of carboxylate ions is used in the coordination to Cu(II). Thermal properties of the complexes **8** and **9** have been studied by TG and DTA and both complexes exhibited high thermal stability while complex **9** are thermally more stable than complex **8**.

Keywords: *[1]benzofuro[3,2-c]pyridine, N-oxide, 1-carbonitrile,* ^1H, ^{13}C *NMR and IR spectra, metal-organic compounds, thermal analysis*

Introduction

The fusion of π-electron rich furan to π -electron poor pyridine ring gives rise to six isomeric furopyridines; the members of all types are known [1–3]. Furopyridines are of chemical interest due to their similarity to quinoline, isoquinoline and benzofuran, which are important ring systems present in many biologically active compounds. The antihypersensitive drug Cicletanine is a furo[3,2-*c*]pyridine derivative. The furopyridine skeleton from which this compound is derived is not associated with any known pharmacological classes [2]. In addition, pharmacophores with potential antipsychotic activity possess thieno- and furo[3,2-*c*]pyridine ring system [4].

In the past one of us has been interested in studying the synthesis and reactivity of various furo[3,2-*c*]pyridines [5–9]. The authors [10, 11] were concentrated on transformations on the pyridine ring of some of this type of compounds. Later on some furo[3,2-*c*]pyridines have been used for preparation Cu(II) and Ni(II) complexes [12]. Furo[3,2-*c*]pyridine and its 2-methyl-, 2,3-dimethyl and benzo [4, 5] derivative were used for the first time as ligands to synthesize potentially new Werner clathrates and their structural characterization, spectral, magnetic and thermal properties of isothiocyanate nickel(II) complexes [13, 14]. Magneto structural correlations in heteroleptic furo[3,2-*c*]pyridine-Ni(II) complexes were published by the research group [15]. Recently two papers dealing with the syntheses and crystal

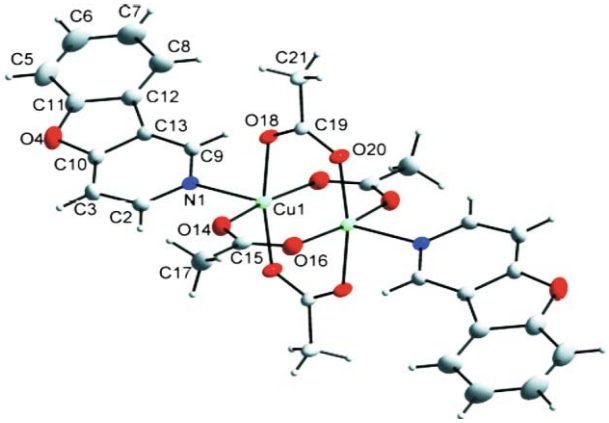

Fig. 1 The molecular structure of the complex compound **8** [16], reproduced with permission

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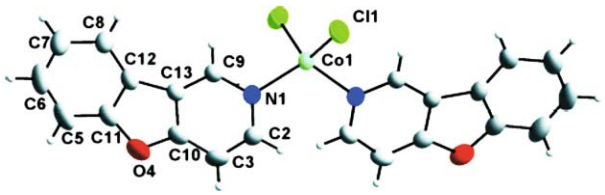
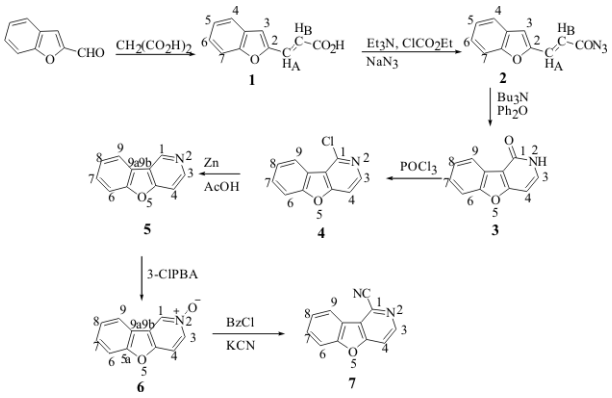


Fig. 2 The molecular structure of the complex compound **9** [17], reproduced with permission

structures of tetra-μ-acetato-bis(1-benzofuro[3,2-*c*]pyridine-copper(II) and bis(1-benzofuro[3,2-*c*]pyridine-κ*N*) dichlorocobalt(II) were published [16, 17] and the crystal structures are given in Figs 1 and 2.

Thermal and spectral studies are very useful techniques for various materials characterization [18–47]. In this paper, which is a continuation of our previous works [6, 8, 10, 11], we report the synthesis of [1]benzofuro[3,2-*c*]pyridine (**5**), its 2-oxide **6** and 1-carbonitrile **7** (Scheme 1) and complexes **8** and **9** together with their spectral and/or thermal properties.



Scheme 1 Synthesis of [1]benzofuro[3,2-*c*]pyridines

Experimental

All solvents were distilled and dried before use. All reagents were commercially available and were used without purification.

*(2E)-3-(1-Benzofuran-2-yl)propenoic acid (**1**)*

A mixture of 1-benzofuran-2-carbaldehyde (5.1 g; 35 mmol), malonic acid (3.7 g; 35 mmol), pyridine (39.3 mL) and piperidine (1.7 mL) was heated on steam bath for 8 h. The reaction mixture was poured onto ice, acidified with 0.5 M hydrochloric acid. The separate precipitate was filtered off and crystallized.

Yield: 11.74 g (88.9%); white crystals, m.p. 222–223°C (ethanol). For $C_{11}H_7N_3O_2$ (M_r=188.18); w_i (calc.): 70.21% C, 4.29% H; w_i (found): 70.41% C, 4.26% H.

*(2E)-3-(1-Benzofuran-2-yl)propenoyl azide (**2**)*

Acid **1** (3.76 g; 20 mmol) suspended in dry acetone (40 mL) was cooled to –10°C and triethylamine (3.2 mL) in dry acetone (5 mL) was added. Then solution of ethyl chloroformate (2.4 mL) in dry acetone (5 mL) was added dropwise to the stirred reaction mixture at temperature lower than 0°C. The reaction mixture was stirred for another 30 min at the same temperature. Solution of sodium azide (2.0 g; 30.8 mmol) in water (10 mL) was added at temperature below 0°C. The mixture was stirred for an additional hour and allowed to warm at room temperature, poured onto crushed ice and precipitate was filtered off, washed with water and crystallized.

Yield: 4.07 g; (95.6%), m.p. 114–116°C white crystals. For $C_{11}H_7N_3O_2$ (M_r=213.19), w_i (calc.): 61.97% C, 3.31% H, 19.71% N; w_i (found): 61.82% C, 3.27% H, 19.78% N.

*[1]Benzofuro[3,2-c]pyridin-1(2H)-one (**3**)*

Azide **2** (8.67 g; 41 mmol) dissolved in toluene (67 mL) was added dropwise into diphenyl ether (35 mL), and tributylamine (10.7 mL) were at 180–200°C for 45 min, while toluene was distilled out. Then the reaction mixture was heated up 215°C for 15 min. After cooling, diethyl ether was added, the precipitate was filtered off and washed with diethyl ether.

Yield: 6.22 g (82.6%), m.p. 207–209°C (ethanol) white crystals.

For $C_{11}H_7NO_2$ (M_r=185.18) w_i (calc.): 71.35% C, 3.81% H, 7.56% N; w_i (found): 71.22% C, 3.78% H, 7.66% N.

*1-Chloro[1]benzofuro[3,2-c]pyridine (**4**)*

A pyridone **3** (4.5 g; 24 mmol) was refluxed in phosphorus oxychloride (8.6 mL) for 4 h. $POCl_3$ was removed at reduced pressure and the ice was added to the residue. The mixture was then made basic with diluted aqueous ammonia. The precipitate was filtered off, washed with water, dried and crystallized.

Yield: 4.71 g (91.2%), m.p. 65–67°C (hexane) white crystals.

*[1]Benzofuro[3,2-c]pyridine (**5**)*

Zinc powder (12.07 g; 185 mmol), was added to **4** (9.0 g; 44 mmol) and acetic acid (15 mL) and mixture was refluxed for 8 h, then filtered and the solvent was distilled off under reduced pressure. The residue was

alkalized with diluted sodium hydroxide solution and extracted with chloroform. The solution was dried with sodium sulfate and the solvent was evaporated. Yield: 4.65 g (62.5%), m.p. 74–76°C (hexane) white crystals.

For $C_{11}H_7NO$ (M_r=169.18) w_i (calc.): 78.09% C, 4.17% H, 8.28% N; w_i (found): 78.12% C, 4.01% H, 8.16% N.

*[1]Benzofuro[3,2-c]pyridine-2-oxide (**6**)*

A mixture of **5** (1.42 g; 8.4 mmol) and 3-chloroperoxybenzoic acid (70%, 3.69 g; 14.6 mmol) in dichloromethane (50 mL) was stirred at room temperature for 4 h. The reaction mixture was filtered and extracted with sodium carbonate solution (10%), and water. The organic layer was dried over sodium sulfate, filtered and solvent was evaporated and residue was crystallized.

Yield: 1.01 g, 65%., m.p. 205–206°C (toluene).

For $C_{11}H_7NO_2$ (M_r=185.18) w_i (calc.): 71.35% C, 3.81% H, 7.56% N; w_i (found): 71.42% C, 3.79% H, 7.38% N.

*[1]Benzofuro[3,2-c]pyridine-1-carbonitrile (**7**)*

A solution of [1]benzofuro[3,2-*c*]pyridin-2-oxide (**6**) (3.42 g, 1.85 mmol) in dichloromethane (10 mL) was added to a solution of potassium cyanide (1.25 g, 19 mmol) in water (2 mL) and then a solution of benzoyl chloride (0.3 mL, 2.15 mmol) in dichloromethane (10 mL) was also dropwise added. After vigorous stirring at room temperature for 2 d, the organic layer of the reaction mixture was separated and aqueous layer was extracted with chloroform. After drying over magnesium sulfate, the combined organic layers were evaporated and residue was purified by column chromatography on silica gel (hexane-ethyl acetate 3:1). The obtained VII was crystallized.

Yield: 3.05 g, (85%), m.p. 135–137°C (hexane) 139–141°C.

For $C_{12}H_6N_2O$ (M_r=194.19) w_i (calc.): 74.22% C, 3.11% H, 14.43% N; w_i (found): 74.32% C, 3.18% H, 14.36% N.

*Tetra-μ-acetato-bis[([1]benzofuro[3,2-c]pyridine) copper(II)] (**8**)*

To a $Cu(CH_3CO_2)_2 \cdot H_2O$ (1.5 mmol) in ethanol (5 mL) was added the solution of the title compound **5** (3.2 mmol) in ethanol (2 mL). Small blue-green crystals were collected after 2 d. These were filtered off, washed with ethanol and crystallized from tetrahydrofuran.

For $C_{30}H_{26}N_2Cu_2O_{10}$ (M_r=701.63) w_i (calc.): 51.35% C, 3.73% H, 3.99% N, 18.11% Cu; w_i (found): 51.43% C, 3.65% H, 3.99% N, 18.15% Cu.

*Bis([1]benzofuro[3,2-c]pyridine-κN)dichlorido-cobalt(II) (**9**)*

To a $CoCl_2 \cdot 6H_2O$ (1 mmol) solution in ethanol (4 mL) was added the solution of **5** (3 mmol) in ethanol (4 mL) at room temperature. Small blue crystals were formed after 3 d, which were filtered off, washed with ethanol and crystallized from tetrahydrofuran.

For $C_{22}H_{14}Cl_2CoN_2O_2$ (M_r=468.21) w_i (calc.): 56.43% C, 3.01% H, 5.98% N, 12.58 Co; w_i (found): 56.67% C, 2.96% H, 5.96% N, 11.96% Co.

Measurements

Melting points were determined using Kofler hot plate.

Elemental analyses were determined using an EAGER 300 at Institute of Inorganic Chemistry, Technology and Materials STU in Bratislava.

FTIR spectra were taken on a FTIR Nicolet NEXUS 470 spectrophotometer using KBr technique (0.5 mg in 300 mg KBr) in the region 4000–400 cm^{-1} at Institute of Physical Chemistry and Chemical Physics, STU in Bratislava. For interpretation of IR spectra following abbreviations are used: *m*=medium band (a value of transmittance: 36–50%) *w*=weak (a value of transmittance: over 50%), without marking are strong bands (a value of transmittance: 0–35%).

NMR spectra were measured in DMSO-d_6 using Varian INOVA 600 (for ^{1}H 599.782 MHz and for ^{13}C 150.830 MHz) spectrometer at Institute of Analytical Chemistry, Department of NMR and MS Spectroscopy, STU in Bratislava. Chemical shifts (δ-scale) are quoted in parts per million and following abbreviations are used: *s*=singlet; *d*=doublet; *t*=triplet, coupling constants (*J*) are given in Hz.

The thermogravimetric and differential thermal analyses were carried out using a Shimadzu DTG-60 thermal analyzer in nitrogen atmosphere. The sample was heated between ambient temperature and 400°C at a heating rate of 10°C min^{-1}.

Results and discussion

Spectral data of all compounds are given in Table 1. (*E*)-3-(1-Benzofuran-2-yl)propenoic acid (**1**) was prepared from 1-benzofuran-2-carbaldehyde under the Doebner's conditions. The obtained acid **1** was converted to the corresponding azide **2**, with (*E*)-configuration at the double bond (see values for *J*(A,B) in Table 1). The azide **2** was cyclized by heating in diphenyl

Table 1 ^{1}H NMR, ^{13}C NMR and FTIR spectral data of synthesized compounds **1**–**7**, complexes **8** and **9**

Compound	Spectral data
1	^{1}H NMR (DMSO-d_6), δ: 12.6 (bs CO_2H); 7.69 (dd, $^{3}J_{(4,5)}$=7.8 Hz, $^{4}J_{(4,6)}$=1.2 Hz, H4); 7.59 (dd, $^{3}J_{(7,6)}$=8.1 Hz, $^{4}J_{(7,5)}$=1.2 Hz, H7); 7.57 (d, $^{3}J_{(B,A)}$=15.6 Hz, H_B); 7.39 (t, $^{3}J_{(6,7)}$=7.8 Hz, H6); 7.34 (s, H3); 7.28 (t, $^{3}J_{(5,6)}$=7.8 Hz, H5); 6.41 (d, $^{3}J_{(A,B)}$=15.6 Hz, H_A). ^{13}C NMR (DMSO-d_6), δ: 167.1 (C=O); 154.9 (C7a); 152.1 (C2); 131.2 (C_B); 128.1 (C3a); 126.7 (C6); 123.6 (C5); 122.2 (C4); 119.4 (C_A); 111.7 (C3); 111.4(C7). IR (KBr), ν_{max}/cm^{-1}: 1671(s); 1630(s); 1451(s); 1419(s); 1304(s); 1268(s); 1200(s); 1127(s); 1007(w); 978(w); 951(s); 882(w); 834(m); 753(s); 738(s); 664(w); 568(m); 456(w).
2	^{1}H NMR (DMSO-d_6), δ: 7.74 (d, $^{3}J_{(B,A)}$=15.5 Hz, H_B); 7.73 (dd, $^{3}J_{(4,5)}$=8.2 Hz, $^{4}J_{(4,6)}$=1.2 Hz, H4); 7.61 (dd, $^{3}J_{(7,6)}$=8.2 Hz, $^{4}J_{(7,5)}$=0.88 Hz, (H7); 7.50 (s, H3); 7.44 (t, $^{3}J_{(6,5)}$=7.2 Hz, H6); 7.30 (t, $^{3}J_{(5,6)}$=7.38 Hz, H5); 6.46 (d, $^{3}J_{(A,B)}$=15.5 Hz, H_A). ^{13}C NMR (DMSO-d_6), δ: 170.9 (C=O); 155.2 (C7a); 151.5 (C2); 133.1 (C_B); 127.9 (C3a); 127.4 (C6); 123.7 (C5); 122.5 (C4); 118.6 (C_A); 114.2 (C3); 111.4 (C7). IR (KBr), ν_{max}/cm^{-1}: 2150(s); 1677(s); 1619(s); 1544(s); 1471(s); 1448(s); 1348(s); 1330(s); 1272(s); 1169(s); 1127(s); 1096(s); 999(s); 951(s); 824(s); 788(s); 687(s); 630(s); 610(m); 544(m); 520(m); 441(m); 402(m).
3	^{1}H NMR (DMSO-d_6), δ: 11.83 (bs, NH); 8.01 (dd, $^{3}J_{(9,8)}$=7.33 Hz, $^{4}J_{(9,7)}$=1.76 Hz, H9); 7.678 (dd, $^{3}J_{(6,7)}$=7.04 Hz, $^{4}J_{(6,8)}$=1.76 Hz, H6); 7.41 (t, $^{3}J_{(7,8)}$=7.33 Hz, H7); 7.407 (t, $^{3}J_{(8,7)}$=7.33 Hz, H8); 7.56 (d, $^{3}J_{(3,4)}$=7.34 Hz, H3); 6.76 (d, $^{3}J_{(4,3)}$=7.34 Hz, H4). ^{13}C NMR (DMSO-d_6), δ: 162.5 (C4a); 159.5 (C1); 154.1 (C5a); 135.2 (C3); 125.7 (C7); 124.2 (C8); 123.6 (C9a); 120.8 (C9); 111.3 (C6); 110.0 (C9b); 94.4 (C4). IR (KBr), ν_{max}/cm^{-1}: 1647(s); 1565(s); 1486(s); 1453(s); 1428(s); 1389(s); 1388(m); 1258(m); 1233(s); 1183(s); 1068(s); 1000(m); 947(m); 906(m); 846m; 788(s); 760(s); 677(m); 653(m); 587(s); 543(s).
4	^{1}H NMR (DMSO-d_6), δ: 8.44 (d, $^{3}J_{(3,4)}$=5.57 Hz, H3); 8.16 (dd, $^{3}J_{(9,8)}$=7.8 Hz, $^{4}J_{(9,7)}$=1.8 Hz, H9); 7.798 (d, $^{3}J_{(4,3)}$=5.57 Hz, H4); 7.782 (dd, $^{3}J_{(6,7)=}$8.3 Hz, $^{4}J_{(6,8)}$=0.88 Hz, H6); 7.64 (t, $^{3}J_{(7,8)}$=7.6 Hz, H7); 7.50 (t, $^{3}J_{(8,7)}$=7.6 Hz, H8). ^{13}C NMR (DMSO-d_6), δ: 161.5 (C4a); 155.1 (C5a); 147.1 (C3); 143.6 (C1); 129.3 (C7); 124.5 (C8); 122.1 (C9); 119.7 (C9b); 118.8 (C9b); 112.0 (C6); 107.6 (C4). IR (KBr), ν_{max}/cm^{-1}: 1589(s); 1561(s); 1457(m); 1428(s); 1331(m); 1294(m); 1261(m); 1233(m); 1186(s); 1152(m); 1016(w); 995(w); 947(s); 842(m); 829(s); 755(s); 614(m); 520(w); 434(w).
5	^{1}H NMR (DMSO-d_6), δ: 9.42 (d, $^{5}J_{(1,4)=}$0.88 Hz, H1); 8.65 (d, $^{3}J_{(3,4)}$=5.8 Hz, H3); 8.25 (dd, $^{3}J_{(9,8)}$=7.6 Hz, $^{4}J_{(9,7)}$=1.2 Hz, H9); 7.785 (dd, $^{3}J_{(6,7)=}$8.2 Hz, $^{5}J_{(6,9)=}$0.88 Hz, H6); 7.78 (dd, $^{3}J_{(4,3)=}$5.8 Hz, $^{5}J_{(4,1)}$=0.88 Hz, H4); 7.60 (t, $^{3}J_{(7,6)}$=8.2 Hz, H7); 7.49 (t, $^{3}J_{(8,7)}$=7.6 Hz, H8). ^{13}C NMR (DMSO-d_6), δ: 160.4 (C4a); 155.7 (C5a); 147.6 (C3); 143.9 (C1); 128.6 (C7); 124.1 (C8); 121.5 (C9); 121.1 (C9b); 120.7 (C9a); 111.9 (C6); 107.5 (C4). IR (KBr), ν_{max}/cm^{-1}: 3063-3037(s); 1590(s); 1577(s); 1481(m); 1463(s); 1446(s); 1331(m); 1293(m); 1266(m); 1243(w); 1207(s); 1186(s); 1162(s); 1106(m); 1009(m); 995(m); 862(s); 838(s); 823(s); 776(s); 751(s); 734(s); 595(s).
6	^{1}H NMR (DMSO-d_6), δ: 9.21 (d, $^{4}J_{(1,3)}$=1.8 Hz, H1); 8.32 (dd, $^{3}J_{(3,4)}$=7.1 Hz, $^{4}J_{(3,1)=}$1.8 Hz, H3); 8.20 (dd, $^{3}J_{(9,8)}$=7.6 Hz, $^{4}J_{(9,7)}$=1.4 Hz, H9); 7.82 (d, $^{3}J_{(4,3)}$=7.1 Hz, H4); 7.76 (dd, $^{3}J_{(6,7)}$=8.2 Hz, $^{4}J_{(6,8)}$=1.7 Hz, H6); 7.64 (t, $^{3}J_{(7,6)=}$8.2 Hz, H7); 7.48 (t, $^{3}J_{(8,9)}$=7.6 Hz, H8). ^{13}C NMR (DMSO-d_6), δ: 156.8 (C5a); 151.3 (C4a); 138.3 (C3); 132.6 (C1); 129.7 (C7); 124.2 (C6); 123.0 (C9b); 122.5 (C9); 120.2 (C9a); 112.2 (C8); 109.9 (C4). IR (KBr), ν_{max}/cm^{-1}: 1661(s); 1470(s); 1440(s); 1308(m); 1288(s); 1205(s); 1158(s); 1098(s); 1010(m); 929(m); 828(s); 769(s); 742(s); 596(s); 526(s); 425(s).
7	^{1}H NMR (DMSO-d_6), δ: 8.81 (d, $^{3}J_{(3,4)}$=5.57 Hz, H3); 8.21 (d, $^{3}J_{(9,8)}$=7.63 Hz, H9); 8.14 (d, $^{3}J_{(4,3)=}$5.57 Hz, H4); 7.89 (d, $^{3}J_{(6,7)=}$8.5 Hz, H6); 7.76 (t, $^{3}J_{(7,8)=}$7.63 Hz, H7); 7.62 ((t, $^{3}J_{(8,7)=}$7.63 Hz, H8). ^{13}C NMR (DMSO-d_6), δ: 160.4 (C4a); 155.8 (C5a); 148.8 (C3); 130.9 (C7); 125.0 (C8); 124.9 (C9b); 124.2 (C1); 121.4 (C9); 118.4 (C9a); 116.2 (CN); 112.6 (C6); 111.4 (C4). IR (KBr), ν_{max}/cm^{-1}: 3093(s); 2227(m); 1627(w); 1591(s); 1567(s); 1483(w); 1458(s); 1422(s); 1336(s); 1295(w); 1263(s); 1231(s); 1182(s); 1109(s); 1072(w); 1015(m); 1005(s); 944(w); 841(s); 806(s); 784(w); 748(s); 641(w); 568(w); 543(m).
8	IR (KBr), ν_{max}/cm^{-1}: 3852(s); 3820(s); 3674(s); 3628(s); 3441(s); 3085(s); 3053(s); 2569(s); 2527(s); 1633(s); 1605(s); 1592(s); 1485(s); 1466(s); 1448(s); 1333(s); 1292(s); 1251(s); 1212(s); 1177(s); 1154(s); 1146(s); 1041(s)878(s); 838(s); 821(s); 774(s); 758(s); 596(s); 574(w); 562(w); 523(w).
9	IR (KBr), ν_{max}/cm^{-1}: 1626(s); 1596(s); 1484(m); 1484(m); 1467(m); 1450(s); 1433(s); 1210(m); 1187(s); 1165(s); 1018(w); 872(s); 840m); 777(s); 757(m); 681(m); 629(s); 598(w); 567(w); 523(w).

ether to [1]benzofuro[3,2-*c*]pyridin-1(2*H*)-one (**3**), which structure was confirmed by spectroscopic data (Table 1). Its FTIR spectra exhibit lactam $\nu_{C=O}$ vibration at 1647 cm^{-1}. This compound was aromatized with phosphorus oxychloride to chloroderivative **4** which was reduced with zinc and acetic acid to the title compound **5**. The position signals of pyridine ring protons (H-3, H-4) were downfield shifted by aromatization of **3** into **4** and **5** (Table 1).

[1]Benzofuro[3,2-*c*]pyridin-2-oxide (**6**) was synthesized by reaction of **5** with 3-chloroperoxybenzoic acid in dichloromethane. Treatment of **6** with benzoyl chloride and potassium cyanide (Reissert–Henze reaction) was shown to produce the corresponding [1]benzofuro[3,2-*c*]pyridine-1-carbonitrile (**7**). This transformation was easily verified by means of infrared spectra (Table 1), loss of *N*-oxide band at 1205 cm^{-1} in the spectra of **7** and an appearance of cyano group absorption at 2227 cm^{-1}. Disappearance of the most downfield signal in the ^{1}H NMR spectra (at 9.21 ppm) of the starting compound **6** also supported the structure of the compound **7** (Table 1). For the assignment of carbon signals in the synthesized compounds 2D-spectra, gCOSY, gHSQCAD and gHMBCAD were used.

*Thermal decomposition of the complexes **8** and **9***

The complexes **8** and **9** are relatively stable and complex **9** is thermally more stable than complex **8**. Thermal decompositions of the complexes **8** and **9** are multistage processes. The subsequent detachment of the ligands was observed.

The TG and DTA curves for the decomposition of $Cu_2(ac)_4(bfp)_2$ (**8**) are shown in Fig. 3. The TG curve indicates that it is thermally stable up to 205°C. Afterwards, the TG curve shows three mass loss steps. The first two simultaneous steps between 205 and 297°C are accompanied by 64.2% mass loss (from the TG curve), and are attributed to the elimination of 2bfp and 2ac and formation of $Cu_2(ac)_2$. The third step took place between 297 and 400°C and is accompanied by 8.40% mass loss. It is attributed, however, to the decomposition of the $Cu_2(ac)_2$. The thermal decomposition reaction of complex **8** can be represented as:

$$Cu_2(ac)_4(bfp)_2 \xrightarrow{205-297\,^\circ C} Cu_2(ac)_2$$

$$Cu_2(ac)_2 \xrightarrow{297-400\,^\circ C} Cu_2(ac)$$

The DTA curve for complex **8** (Fig. 3) shows an endothermic peak and two exothermic peaks at 230, 240 and 390°C ascribed to the loss of 2bfp, 2ac and ac, respectively.

The TG and DTA curves of $CoCl_2(bfp)_2$ (**9**) are presented in Fig. 4. The TG curve for this complex indicates that it is thermally stable up to 220°C, where

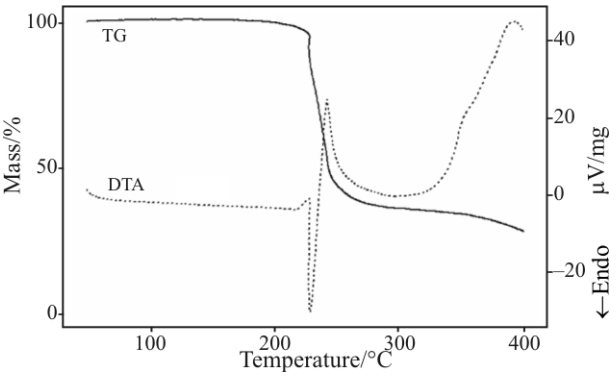


Fig. 3 TG and DTA curves of $Cu_2(ac)_4(bfp)_2$ (**8**)

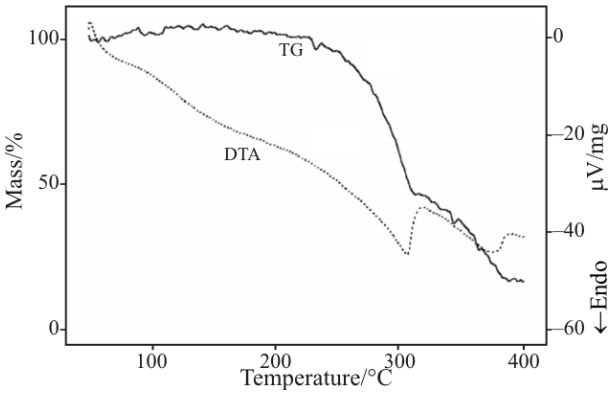


Fig. 4 TG and DTA curves of $CoCl_2(bfp)_2$ (**9**)

the decomposition process commences and follows by two mass loss steps. The first step between 220 and 316°C is accompanied by 54.20% mass loss and attributed to the decomposition of the complex to $CoCl_2(py)$, where py=pyridine. The second step between 316 and 400°C is accompanied by 29.00% mass loss. It is attributed to the decomposition of $CoCl_2(py)$ to Co. The thermal reaction of the complex **9** can be represented as:

$$CoCl_2(bfp)_2 \xrightarrow{220-316\,^\circ C} CoCl_2(py)$$

$$CoCl_2(py) \xrightarrow{316-400\,^\circ C} Co$$

The DTA curve for the complex **9** (Fig. 4) shows two endothermic peaks at 305 and 380°C attributed to the decomposition of 2bfp and $Cl_2(py)$, respectively.

Conclusions

The title compound [1]benzofuro[3,2-*c*]pyridine (**5**) was prepared by five-step synthesis and was used for the preparation of complexes $Cu_2(ac)_4(bfp)_2$ (**8**) and $CoCl_2(bfp)_2$ (**9**). The structures of **8** and **9** were proved by X-ray analysis (Figs 1 and 2). The single crystal structural data are presented in [16, 17].

The complexes **8** and **9** showed high thermal stability. The decompositions of these compounds were initiated by the elimination of neutral ligand bfp. Then the decomposition of anionic ligands occurred (on the TG curves). The thermal stability of the complexes can be ordered in the sequence: **8**<**9**. The stoichiometry of thermal decomposition can also be influenced by the changes of experimental conditions, origin and preparation history [48, 49]. The spectral properties of the compounds have been studied by means of FTIR and NMR spectra. Infrared spectral data suggested that both oxygen atom of carboxylate ions is used in the coordination to Cu(II) which is also confirmed by single crystral structure studies [16].

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