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Synthesis and characterization of triethanolamine complexes with cobalt(II) and zinc(II) cinnamates

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Experimental section

*Synthesis of complexes **1-3***

*Synthesis of complex **1***. TEA (4.02 mmol, 0.60 g) solution in methanol (130 ml) was added to the cobalt (II) cinnamate, $Co(C_9H_7O_2)_2{\cdot}2H_2O$ (2.01 mmol, 0.78 g), with constant stirring. The resultant mixture was heated to 70 °C with constant stirring for 3 h. After the reaction, the dark cherry-colored solution was evaporated at reduced pressure to form the product – complex **1** as a light brown powder, which was washed with diethyl ether and air-dried. The yield of complex **1** was 1.23 g (94 %). Crystals of complex **1** were isolated from a solution in methanol by slow evaporation at room temperature. Elemental analysis, calculated for $C_{30}H_{44}N_2O_{10}Co$, %: C 55.30; H 6.81; N 4.30, found, %: C 55.78; H 7.05; N 4.39. M.p. = 146 °C.

*Synthesis of complex **2***. Zinc(II) cinnamate, $Zn(C_9H_7O_2)_2{\cdot}2H_2O$, (0.67 mmol, 0.27 g) was added in small portions to the methanol solution of TEA (0.67 mmol, 0.10 g) with constant stirring. The resulting reaction mixture was boiled for 3 hours with constant stirring. The reaction product, complex **2**, was isolated as a colorless powder by slow evaporation of the solvent at room temperature and dried in air. The product yield was 0.33 g (97 %). Elemental analysis, calculated for $C_{24}H_{29}ZnNO_7$, %: C 56.65; H 5.74; N 2.75; found, %: C 57.11; H 5.98; N 2.31. M.p.= 130 °C.

*Synthesis of complex **3***. Complex **3** was obtained similarly to complex **2** by the interaction of TEA (1.68 mmol, 0.25 g) with zinc cinnamate (0.84 mmol, 0.33 g) in methanol. The product yield was 0.52 г (95 %). Elemental analysis, calculated for $C_{30}H_{44}ZnN_2O_{10}$, %: C 54.76; H 6.74; N 4.26; found, %: C 55.33; H 6.80; N 3.82. M.p. = 115 °C.

Cobalt(II) and zinc(II) cinnamates were previously prepared by adding an aqueous alcohol solution of sodium cinnamate to an aqueous solution of cobalt (II) nitrate or zinc (II) chloride (molar ratio of reagents 2: 1) with constant stirring and heating (T = 60-70 °C). After mixing the solutions, precipitation was almost immediately observed. The reaction product was filtered and repeatedly washed with water, dried in air. Yields of cobalt (II) and zinc (II) cinnamates were 81% and 88 %, respectively.

Methods and Instruments

IR spectra of **1-3** were recorded with a Nicolet 8700 (Thermo Scientific) FTIR spectrometer, using pressed KBr pellets. Elemental analysis was obtained on an Elemental analyzer Euro EA3028-NT for the simultaneous determination of C, H, N. Thermal stability of complexes **1-3** was carried out using a simultaneous thermal analyzer STA 429 CD (NETZSCH) with a platinum-rhodium holder for samples. For analysis of decomposition products a quadrupole mass spectrometer QMS 403 C (NETZSCH) was used, which allows to analyze products of thermal decomposition in the range from 1 to 121 atomic mass units. The melting point of complexes **1-3** was additionally defined by SMP10 Melting point apparatus.

Electrospray ionization mass spectra were recorded with a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source in a *m/z* range from 50 to 3000. The parameters of the ESI source were as follows: capillary voltage 4500 V, end plate offset voltage −500 V, nebulizer pressure 0.4 bar, drying temperature 180°C, dry gas flow rate 4 L/min.

NMR spectra of complexes **2** and **3** in DMSO-d_6 solutions were registered on a Bruker Avance III spectrometer [400.13 (^{1}H), 100.613 MHz (^{13}C)]. Chemical shifts presented below are relative to residual signals of dimethyl sulfoxide (2.50 ppm for ^{1}H and 39.52 ppm for ^{13}C)[†].

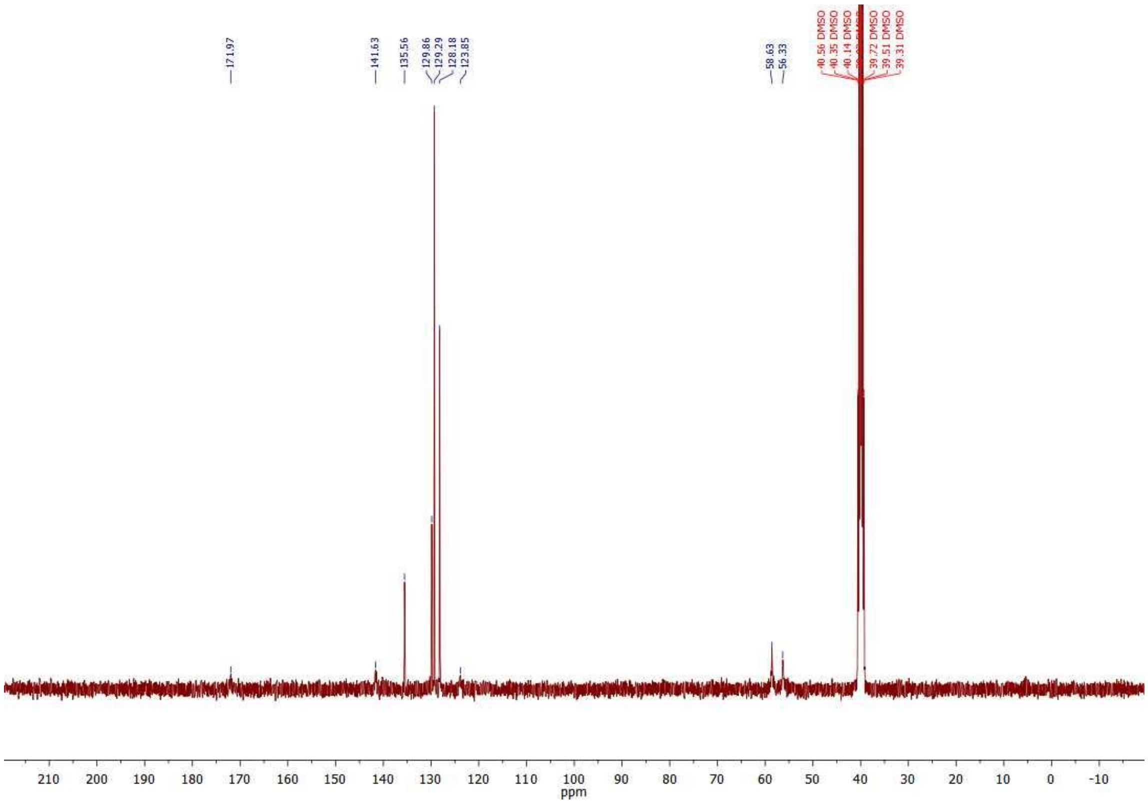


Figure S1. ^{13}C NMR spectrum (DMSO-d6, δ, ppm) of complex **2:** 56.3 ($N\underline{C}H_2$), 58.6 ($\underline{C}H_2OH$), 123.9 ($PhCH\underline{C}HCO_2^-$) 128.2 ($C_{Ar}H$), 129.3 ($C_{Ar}H$), 129.9 ($C_{Ar}H$), 135.6 ($C_{Ar}H$), 141.6 ($Ph\underline{C}HCHCO_2^-$), 172.0 ($PhCHCH\underline{C}O_2^-$)

[†] ^{1}H NMR spectra of complexes **2** and **3** were characterized by low resolution, namely two broadened singlets of protons of $NC\underline{H_2}$ and $C\underline{H_2}OH$ groups of triethanolamine were observed instead of two triplets.

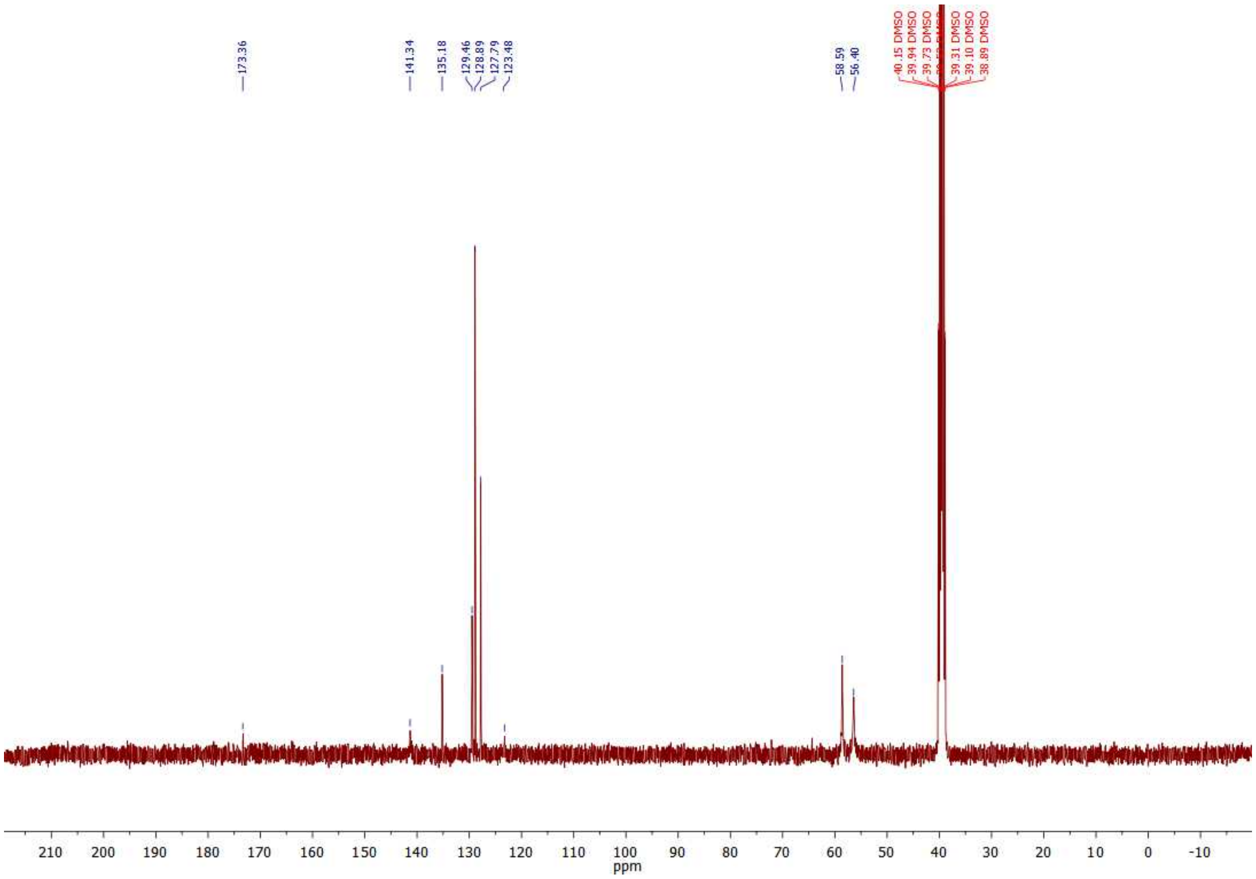
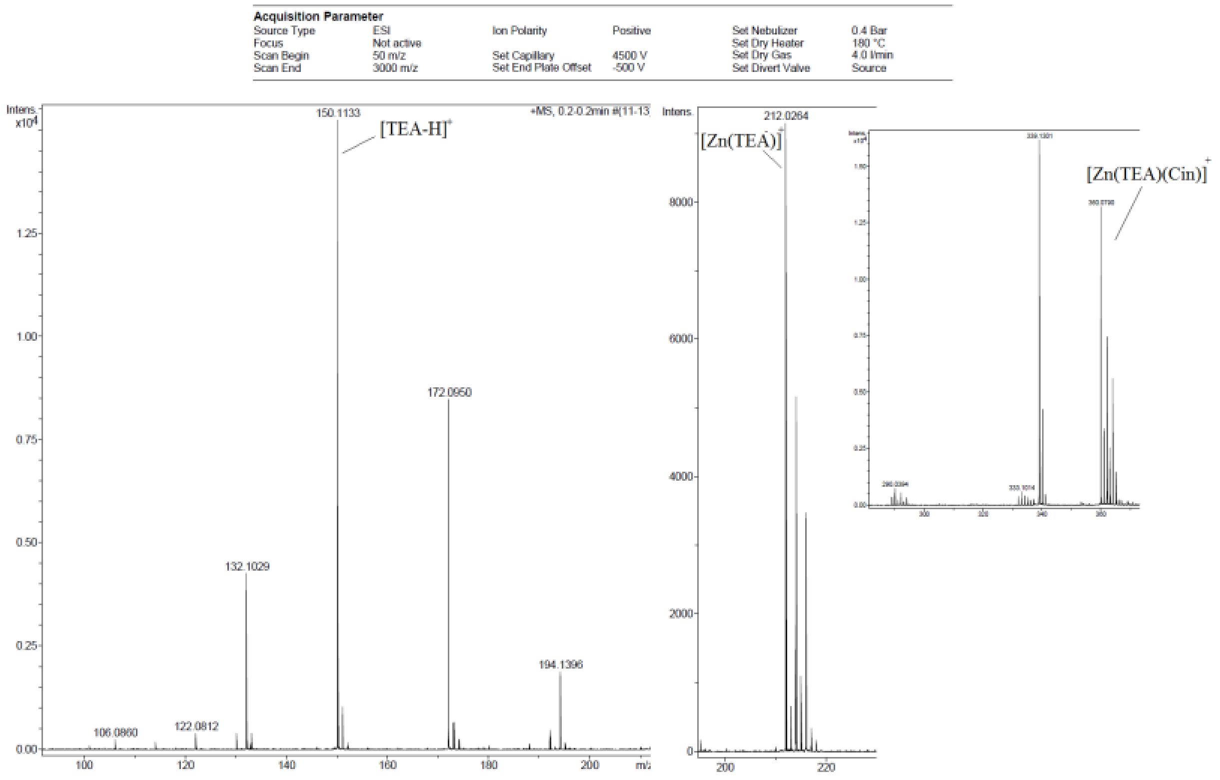


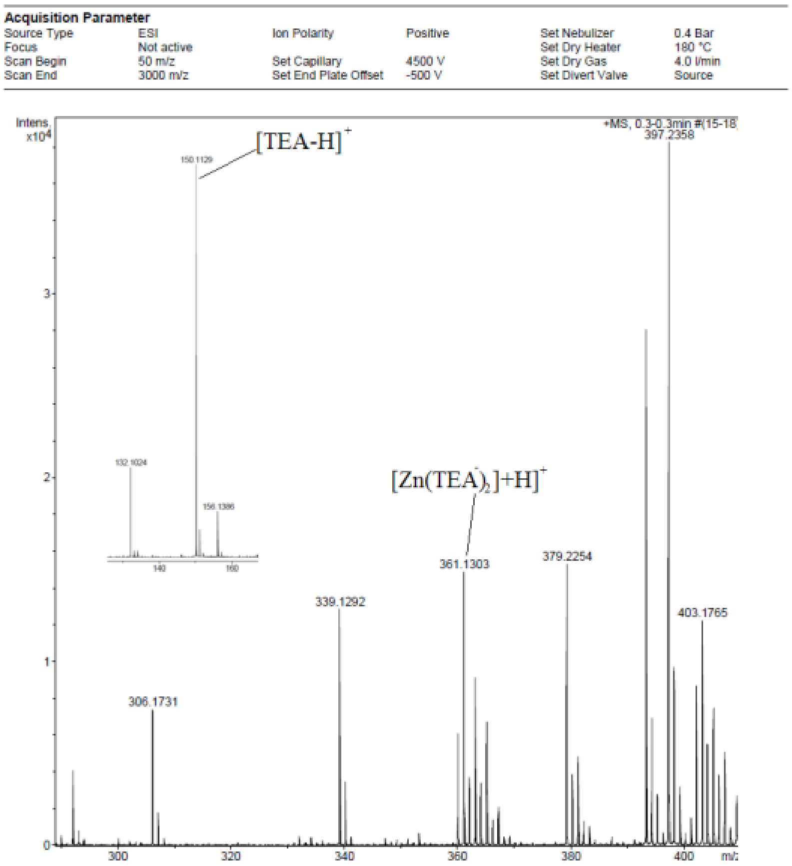
Figure S2. ^{13}C NMR spectrum (DMSO-d6, δ, ppm) of complex **3**: 56.4 (N$\underline{C}H_2$), 58.6 ($\underline{C}H_2OH$), 123.5 ($PhCH\underline{C}HCO_2^-$) 127.8 ($C_{Ar}H$), 128.9 ($C_{Ar}H$), 129.5 ($C_{Ar}H$), 135.2 ($C_{Ar}H$), 141.3 ($Ph\underline{C}HCHCO_2^-$), 173.4 ($PhCHCH\underline{C}O_2^-$)



Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

Figure S3. ESI mass spectrum of complex **2**



Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source

Figure S4. ESI mass spectrum of complex **3**

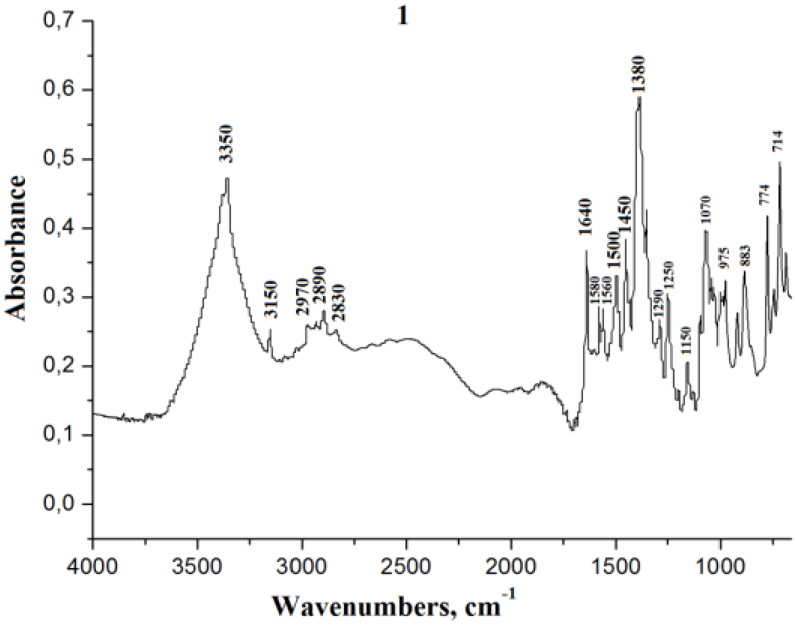


Figure S5. IR spectrum of complex **1**

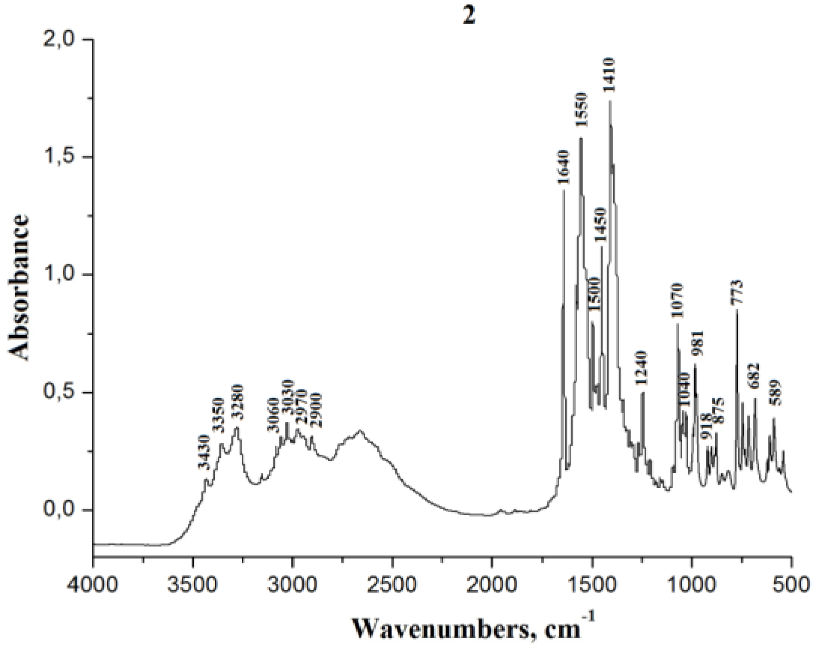


Figure S6. IR spectrum of complex **2**

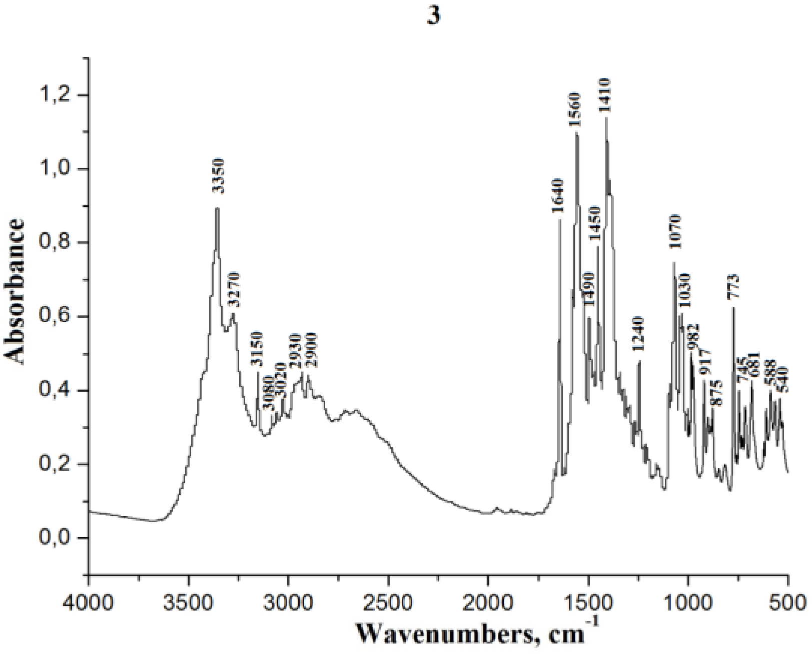


Figure S7. IR spectrum of complex **3**

Table S1. Bond lengths, valence and torsion angles for complex **1**

Bond	d, Å	Bond	d, Å
Co1-O1	2.0832(19)	N6-C28	1.486(3)
Co1-O4	2.0926(19)	N6-C16	1.495(4)
Co1-N6	2.158(2)	N6-C25	1.490(3)
O1-C17	1.441(3)	C1-C16	1.523(4)
O4-C29	1.431(3)	C17-C25	1.520(4)
O8-C1	1.382(4)	C28-C29	1.523(4)

O2-C12	1.276(4)	C11-C15	1.334(4)
O9-C12	1.253(4)	C11-C21	1.467(4)
C23-C38	1.389(4)	C12-C15	1.495(4)
C35-C38	1.389(5)	C18-C36	1.385(4)
C35-C36	1.390(4)	C18-C21	1.401(4)
		C21-C23	1.399(4)
Valence angle	**ω (º)**	**Angle**	**ω (º)**
O1-Co1-O4*	88.13(8)	C28-N6-Co1	107.19(16)
O1-Co1-O4	91.87(8)	C16-N6-Co1	108.37(16)
O1-Co1-N6	81.61(8)	C25-N6-Co1	105.77(16)
O1-Co1-N6*	98.39(8)	O8-C1-C16	112.4(2)
O4-Co1-N6*	97.41(8)	N6-C16-C1	118.2(2)
O4-Co1-N6	82.58(8)	O1-C17-C25	110.1(2)
C17-O1-Co1	114.37(15)	N6-C25-C17	112.5(2)
C29-O4-Co1	110.48(16)	N6-C28-C29	112.6(2)
C28-N6-C16	111.0(2)	O4-C29-C28	110.4(2)
C28-N6-C25	113.3(2)	C15-C11-C21	128.0(3)
C16-N6-C25	110.9(2)	O9-C12-O2	124.5(3)
C11-C15-C12	121.0(3)	O9-C12-C15	119.5(3)
C36-C18-C21	120.6(3)	O2-C12-C15	115.9(3)
C23-C21-C18	118.1(3)	C38-C35-C36	119.8(3)
C23-C21-C11	118.8(3)	C18-C36-C35	120.5(3)
C18-C21-C11	123.1(3)	C35-C38-C23	119.5(3)
C38-C23-C21	121.5(3)		
Torsion angle	**ω (º)**	**Angle**	**ω (º)**
O4-Co1-O1-C17	81.14(17)	O1-Co1-N6-C16	-140.13(17)
O4-Co1-O1-C17*	-98.86(17)	O4-Co1-N6-C16	126.87(17)
N6-Co1-O1-C17	178.92(17)	O4-Co1-N6-C16*	-53.13(17)
O1-Co1-O4-C29*	116.25(17)	N6-Co1-N6-C16	-18(29)
O1-Co1-O4-C29	-63.75(17)	O1-Co1-N6-C25*	158.89(17)
O4-Co1-O4-C29	-155(18)	O1-Co1-N6-C25	-21.11(17)
N6-Co1-O4-C29*	-162.46(17)	O4-Co1-N6-C25	-114.12(18)
N6-Co1-O4-C29	17.54(17)	O4-Co1-N6-C25*	65.88(18)
O1-Co1-N6-C28*	-79.97(18)	N6-Co1-N6-C25	101(29)
O1-Co1-N6-C28	100.03(18)	C28-N6-C16-C1	-57.4(3)
O4-Co1-N6-C28	7.02(17)	C25-N6-C16-C1	69.4(3)
O4-Co1-N6-C28*	-172.98(17)	Co1-N6-C16-C1	-174.9(2)
N6-Co1-N6-C28	-138(29)	O8-C1-C16-N6	-72.9(3)
O1-Co1-N6-C16*	39.87(17)	Co1-O1-C17-C25	23.1(3)
C16-N6-C25-C17	157.6(2)	C28-N6-C25-C17	-76.8(3)
Co1-N6-C25-C17	40.3(3)	Co1-N6-C28-C29	-29.6(3)
O1-C17-C25-N6	-43.1(3)	Co1-O4-C29-C28	-38.4(3)
C16-N6-C28-C29	-147.8(2)	N6-C28-C29-O4	46.5(3)
C25-N6-C28-C29	86.6(3)	C21-C11-C15-C12	-179.9(2)
O2-C12-C15-C11	171.3(3)	O9-C12-C15-C11	-8.2(4)
C36-C18-C21-C23	1.9(4)	C11-C21-C23-C38	176.3(2)
C36-C18-C21-C11	-176.0(3)	C21-C18-C36-C35	0.4(5)
C15-C11-C21-C23	177.4(3)	C38-C35-C36-C18	-2.9(5)
C15-C11-C21-C18	-4.7(4)	C36-C35-C38-C23	3.1(4)
C18-C21-C23-C38	-1.7(4)	C21-C23-C38-C35	-0.8(4)

* Atom refers to a second TEA ligand

Table S2. Results of testing of compounds against micromycetes - destructors of materials

Compound	Test objects. Average score* of micromycetes growth		
	A. niger	*C. cladosporioides*	*P. brevicompactum*
Complex **1**	1	1	1
[TEAH](Cin)	5	5	5

*Average score (GOST 9.048–89): 0 - germination of spores and conidia are not detected by microscopy; 1 - germinated spores and slightly developed mycelium are visible using microscope; 2 - developed mycelium is visible using microscope, sporulation is possible; 3 - the mycelium and (or) sporulation are barely visible to the unaided eye, but are clearly visible under the microscope; 4 - development of fungi covering less than 25% of the test surface is clearly visible to the unaided eye; 5 - development of fungi covering more than 25% of the test surface is clearly visible to the unaided eye.

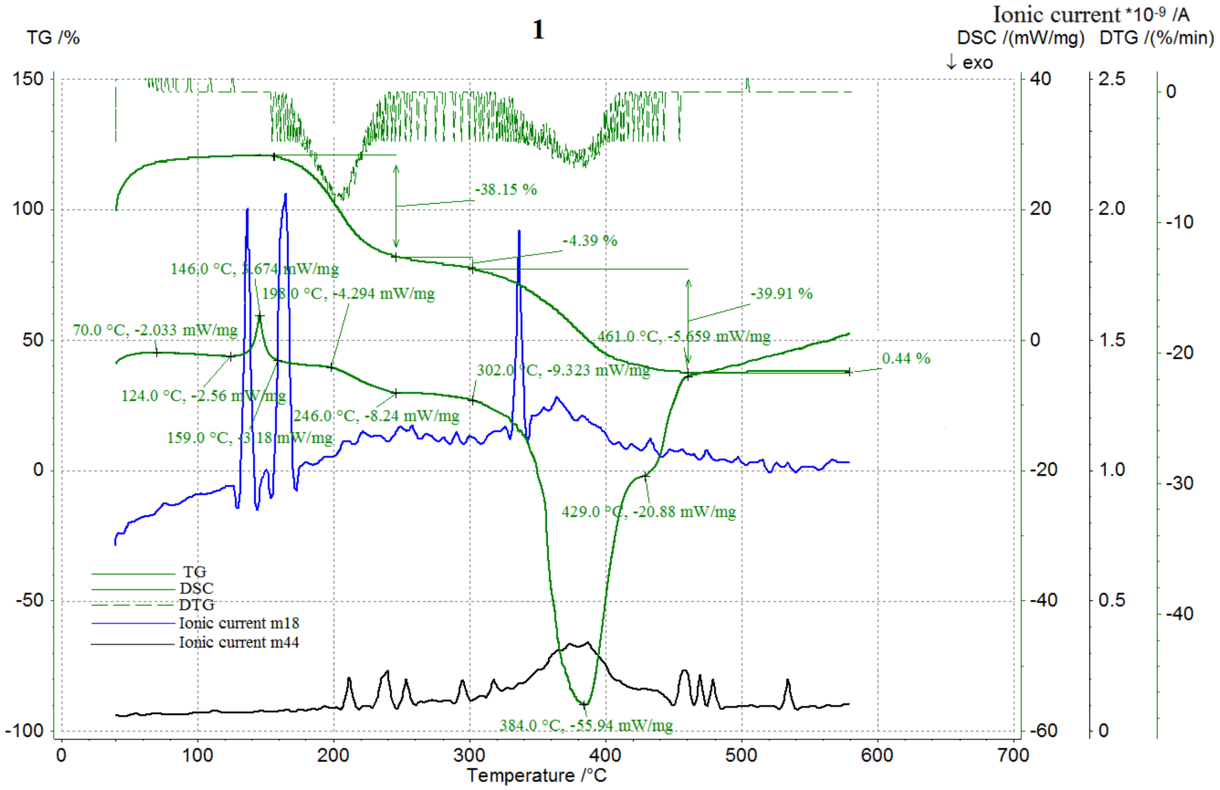


Figure S8. TG, DSC, DTG and IC curves of complex **1** obtained by heating samples from 40 to 600 °C at a heating rate of 10 ºC/min

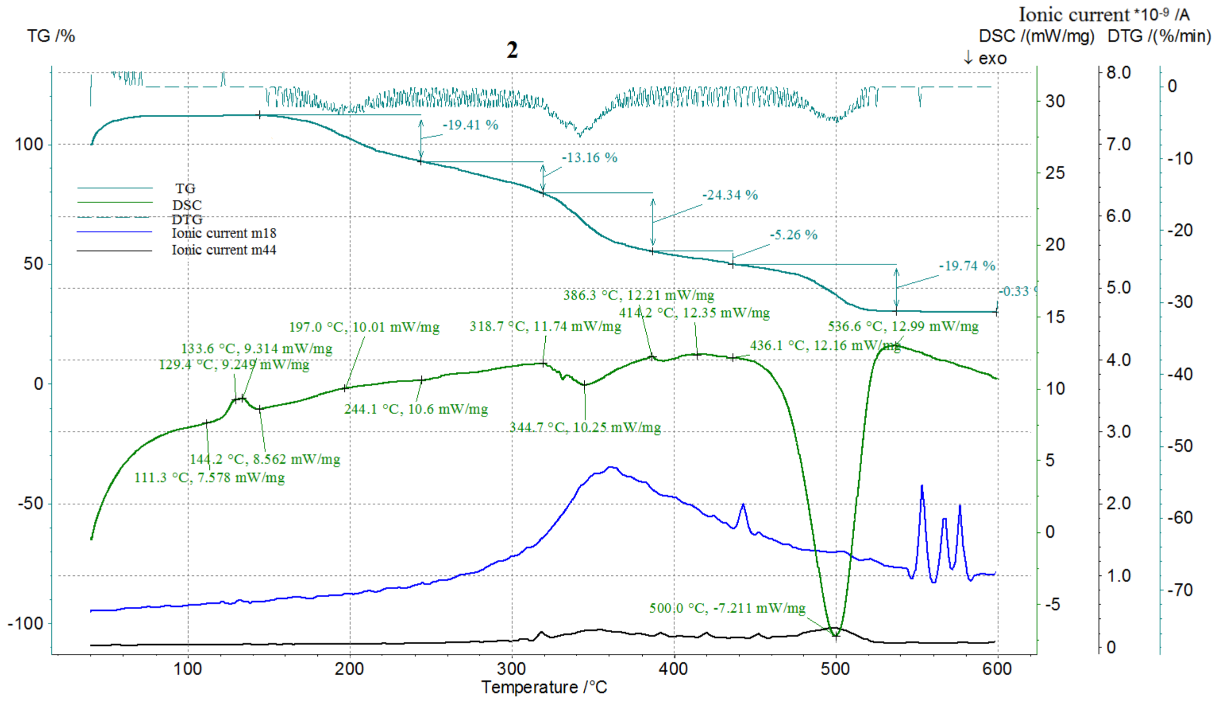


Figure S9. TG, DSC, DTG and IC curves of complex **2** obtained by heating samples from 40 to 600 °C at a heating rate of 10 ºC/min

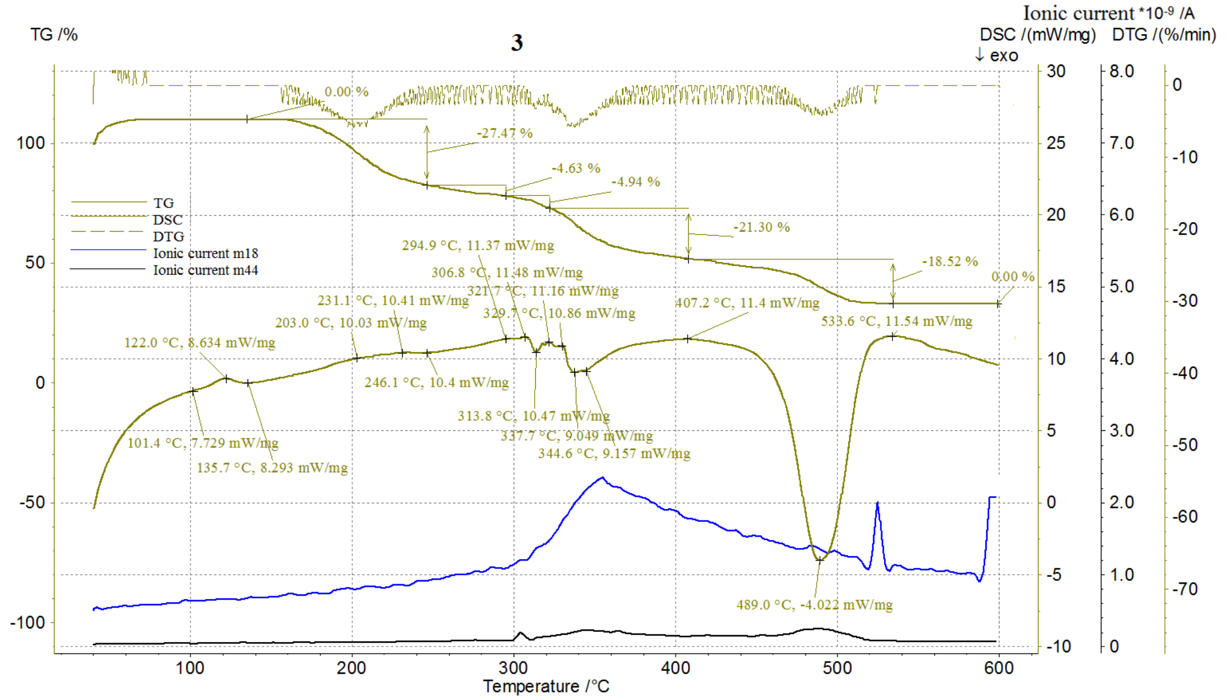


Figure S10. TG, DSC, DTG and IC curves of complex **3** obtained by heating samples from 40 to 600 °C at a heating rate of 10 ºC/min

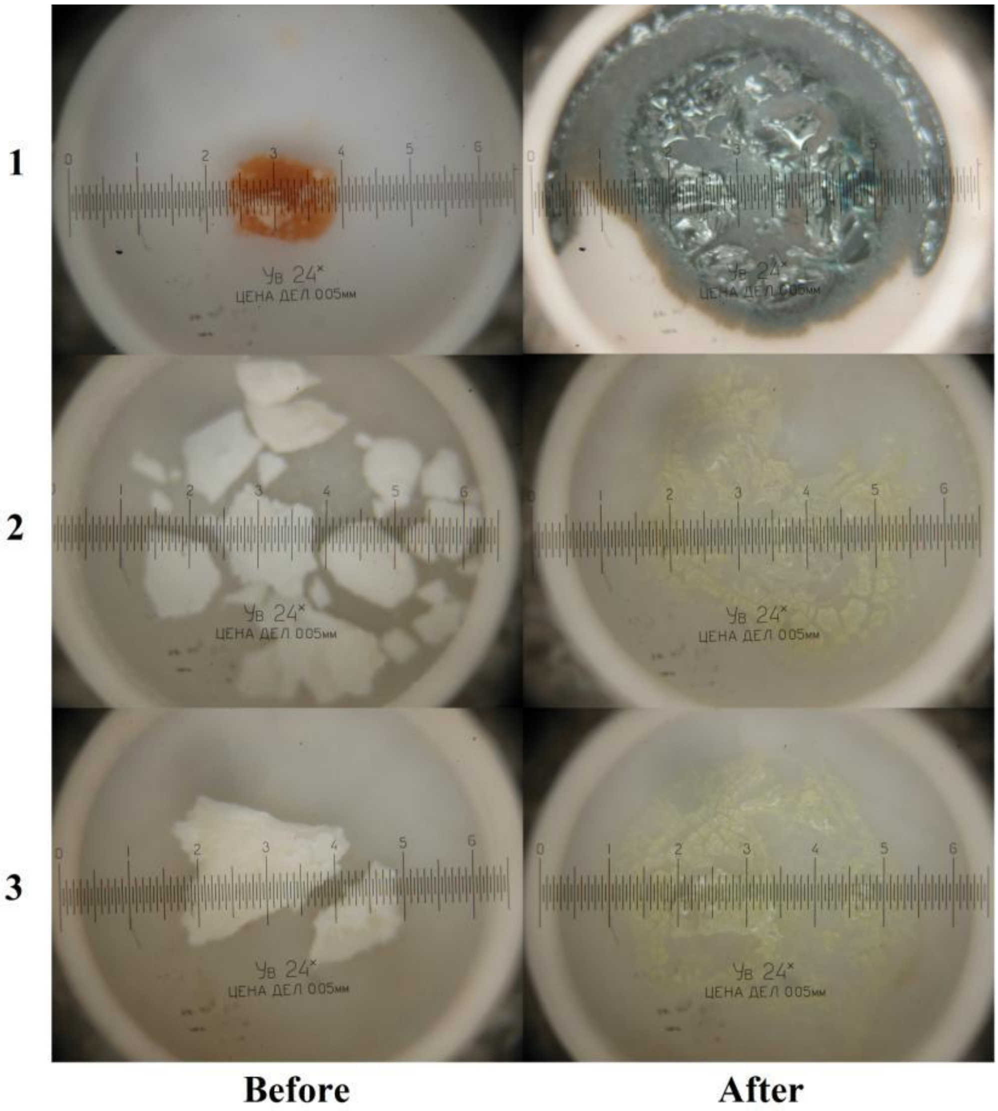


Figure S11. Microphotographs of samples **1-3** before and after heating to 600 °C at 24 – fold magnification, 0.05 mm scale interval