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Ring-opening polymerization of octamethylcyclotetrasiloxane using trifluoroacetate 3d metal complexes

Fedor V. Drozdov, Tatyana Yu. Glazunova, Nikita L. Shikut', Nina V. Demchenko, Ekaterina A. Kurzina, Paulina Kalle and Aziz M. Muzafarov

Experimental details

1. Chemicals and methods

Nickel carbonate ($NiCO_3$) (powder, analytical grade purity), basic cobalt carbonate ($Co(OH)_2 \cdot CoCO_3 \cdot xH_2O$) (powder, reagent grade purity), sodium fluoride (NaF) (powder, reagent grade purity), trifluoroacetic acid (HTFA) (99.9%, Acros Organics), octamethylcyclotetrasiloxane (98%, Penta-91) were used as the precursors.

Gel permeation chromatography (GPC) analysis was performed on a Shimadzu LC-10A series chromatograph (Japan) equipped with an RID-10A refractometer and SPD-M10A diode matrix detectors. Analytical separation was performed with a Phenomenex column (USA) with a size of 7.8 mm × 300 mm filled with Phenogel sorbent with a pour size of 15-500 Å.

X-Ray diffraction data were acquired on a Bruker SMART APEX II single crystal diffractometer (Mo K_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). Absorption correction based on measuring the equivalent reflections {multi-scan} was carried out. The structures were solved by direct methods and refined by the full-matrix least-squares method with respect to F2 (SHELX-2014 software package [S1]) in the approximation of anisotropic thermal vibrations for all non-hydrogen atoms. The positions of hydrogen atoms were calculated geometrically and refined according to the riding model. The crystallographic characteristics and parameters of the survey are given in Table S2.

X-Ray fluorescence analysis (XRF) was performed on a Mistral-M1 spectrometer (Bruker) equipped with a microfocus X-ray tube with high beam brightness (accelerating voltage 50 kV) and an XFlash energy-dispersive silicon detector. X-Ray radiation was focused into a spot measuring 100 μm in diameter. A video microscope with a sighting function and a motorized vertical table provided accurate positioning of the sample. This equipment allows one to determine elements with charge number $z > 22$, whereas the characteristic radiation of elements with smaller ordinal numbers is absorbed by air. The detection limit of this method is about 0.005 weight %. The concentrations were determined from the areas of individual peaks, based on the model of

fundamental parameters and using the built-in XSpect program and the spectra of standard substances included in the database program.

2. Synthesis of trifluoroacetate complexes

Homonuclear trifluoroacetate complexes of d-metals were obtained just prior to polymerization according to the procedures described in the literature [S2]. The purity of the complexes obtained was proved by the XRF method.

The cobalt, nickel and zinc trifluoroacetate tetrahydrates of general formula **$M(TFA)_2 \cdot 4H_2O$ (M = Co, Ni, Zn)** were obtained from basic carbonates of the corresponding metals (3 g, 0.028 mol for Co, Zn, 0.024 mol for Ni), followed by recrystallization of the products from an aqueous solution of trifluoroacetic acid (15 ml of 50% solution, 0.068 mol). The yields of products were close to 100%.

$$M(CO_3)_x(OH)_y + TFA + H_2O \rightarrow M(TFA)_2 \cdot 4H_2O + CO_2$$

The trinuclear acid trifluoroacetates of cobalt and nickel **$M_3(TFA)_6(HTFA)_6 \cdot HTFA$ (M=Co, Ni)** were synthesized by recrystallization of the corresponding trifluoroacetate tetrahydrates (1 g, 2.8 mmol) from anhydrous trifluoroacetic acid (7 ml, 0.096 mol) in a vacuum desiccator over P_4O_{10}. The yields were close to 100%.

$$3\ M(TFA)_2 \cdot 4H_2O + 7\ TFA \rightarrow M_3(TFA)_6(HTFA)_6 \cdot TFA + 4H_2O$$

Tricyclic sodium fluoro(trifluoroaceto)metallates **$Na[M_3(\mu_3\text{-}F)(TFA)_6(HTFA)_3]$ (M = Co, Ni)** were obtained by recrystallization of a stoichiometric mixture of the tetrahydrate of the corresponding metal (1 g, 2.8 mmol) with sodium fluoride (0.039 g, 0.93 mmol) from anhydrous trifluoroacetic acid (7 ml, 0.096 mol) in a vacuum desiccator over P_4O_{10}. The yields were close to 100%.

$$3\ M(TFA)_2 \cdot 4H_2O + NaF + 3\ HTFA \rightarrow Na[M_3(\mu_3\text{-}F)(TFA)_6(HTFA)_3] + 12H_2O$$

Zinc oxotrifluoroacetate **$Zn_4(\mu_4\text{-}O)(TFA)_6$** was obtained by thermal decomposition of zinc trifluoroacetate tetrahydrate (1 g, 2.8 mmol) followed by sublimation in a dynamic vacuum [S3]. The yield was 80%.

$$4\ Zn(TFA)_2 \cdot 4H_2O \rightarrow Zn_4(\mu_4\text{-}O)(TFA)_6 + 2\ HTFA + 3H_2O$$

The heteronuclear trifluoroacetate complexes **$[ZnCo(CF_3COO)_4(CF_3COOH)_2]_n$** and **$[ZnZn_{0.4}Ni_{0.6}(TFA)_4(HTFA)_2]_n$** were synthesized by simultaneous recrystallization of equimolar amounts of zinc trifluoroacetate (0.5 g, 1.4 mmol) and cobalt (nickel) tetrahydrates (0.5 g, 1.4 mmol) from anhydrous trifluoroacetic acid (7 ml, 0.096 mol) in a vacuum desiccator over P_4O_{10}. The compounds have the form of leaf-like red and green crystals, respectively, that are unstable with respect to the air moisture. The reaction yield is close to 100% in the case of the cobalt derivative and to 60% in the case of the nickel derivative.

$$n Zn(TFA)_2 \cdot 4H_2O + n Co(TFA)_2 \cdot 4H_2O + 2n\ HTFA \rightarrow [ZnCo(TFA)_4(HTFA)_2]_n + 2nH_2O$$

or

$$1.4n\ Zn(TFA)_2 \cdot 4H_2O + 1.4n\ Ni(TFA)_2 \cdot 4H_2O + 3.02n\ HTFA \longrightarrow$$
$$[ZnZn_{0.4}Ni_{0.6}(TFA)_4(HTFA)_2]_n + 0.22n\ Ni_3(TFA)_6(HTFA)_6 \cdot HTFA + 2.8nH_2O$$

3. General method for cationic polymerization of octamethylcyclotetrasiloxane using trifluoroacetate complexes

Cationic polymerization was carried out by direct reaction of an acid or complex (1 eq. = 0.01 mol of TFA residue per 1 eq. of Si-O bond) with dried octamethylcyclotetrasiloxane (2.96 g, 0.01 mol) with constant stirring at 75 °C for 35 hours under argon atmosphere. The resulting reaction mixture was filtered to remove inorganic impurities using Schott filter under vacuum. Molecular weight characteristics of the substances obtained were analyzed by GPC. The average molecular weights were determined using calibration based on polystyrene standards. Samples of the reaction mixture were taken every 5 hours to study the rate of polymerization. The reaction was considered completed while molecular weight did not change further.

References

[S1] G. M. Sheldrick, *Acta Crystallogr*., 2008, **64**, 112.

[S2] I. V. Morozov, E. V. Karpova, T. Yu. Glazunova, A. I. Boltalin, M. A. Zakharov, D. S. Tereshchenko, A. A. Fedorova, S. I. Troyanov, *Russ. J. Coord. Chem*., 2016, **42**, 647 (*Koord. Khim*., 2016, **42**, 609).

[S3] N. S. Shikut', *Trifluoroacetate complexes of 3d-metals as catalysts of polymerization with opening of cyclosiloxanes. Proceedings of Lomonosov-2018 Conference*, Maks-Press, Moscow, 2018.

Table S1 Basic crystallographic parameters and analysis conditions for $[ZnCo(CF_3COO)_4(CF_3COOH)_2]_n$ **1** and $[ZnZn_{0.4}Ni_{0.6}(CF_3COO)_4(CF_3COOH)_2]_n$ **2**.

	1	**2**
Formula weight	1604.84	1604.40
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.8458(8)	8.8234(4)
b (Å)	15.1341(13)	15.0715(6)
c (Å)	18.2036(16)	18.1278(8)
β (°)	100.7850(10)	101.0720(10)
V (Å^3)	2393.9(4)	2365.80(18)
Z	4	4
D_{calc}, (g cm^{-3})	2.226	2.252
μ(Mo K_α) (cm^{-1})	1.892	2.009
Crystal size, mm	0.400x0.250x0.100	0.300x0.200x0.080
Temperature, K	150(2)	120(2)
θ(max)	25.999	28.0
Total number of reflexes	19756	28040
Number of independent reflexes / Number of reflexes with F^{o}2	4693/387	6914/387
wR_2	0.1591	0.1511
R_1	0.0637	0.0603
Δρ max. / min. (ē Å^{-3})	0.140	0.150

Table S2 Bond lengths and angles in the chain structures of $[ZnCo(CF_3COO)_4(CF_3COOH)_2]_n$ **1** and $[ZnZn_{0.4}Ni_{0.6}(CF_3COO)_4(CF_3COOH)_2]_n$ **2**.

	1, Å	**2,** Å		**1,** º	**2,** º
M1-O(10)	2.007(4)	1.999(3)	O(10)-M1-O(6)	94.06(17)	95.05(12)
M1-O(11)	2.072(4)	2.062(3)	O(11)-M1-O(6)	92.17(15)	92.10(11)
M1-O(6)	2.082(4)	2.053(3)	O(10)-M1-O(8)	96.86(17)	97.67(12)
M1-O(8)	2.098(4)	2.066(3)	O(11)-M1-O(8)	80.21(16)	80.21(11)
M1-O(4)	2.123(4)	2.101(3)	O(6)-M1-O(8)	103.62(17)	103.16(12)
M1-O(2)	2.126(4)	2.106(3)	O(10)-M1-O(4)	89.86(16)	88.69(12)
M2-O(9)	1.929(4)	1.920(3)	O(11)-M1-O(4)	91.84(16)	91.93(11)
M2-O(5)	1.939(4)	1.941(3)	O(6)-M1-O(4)	87.95(16)	88.76(11)
M2-O(7)	1.940(5)	1.950(3)	O(10)-M1-O(2)	86.33(17)	84.97(12)
M2-O(12)	1.966(4)	1.964(3)	O(11)-M1-O(2)	87.73(15)	88.04(11)
			O(8)-M1-O(2)	85.05(17)	85.38(12)
			O(4)-M1-O(2)	83.25(16)	82.59(11)
			O(9)-M2-O(5)	119.40(19)	118.67(14)
			O(9)-M2-O(7)	111.5(2)	111.56(14)
			O(5)-M2-O(7)	109.0(2)	108.97(14)
			O(9)-M2-O(12)	108.47(17)	109.52(12)
			O(5)-M2-O(12)	107.08(16)	107.09(12)
			O(7)-M2-O(12)	99.36(16)	99.17(12)

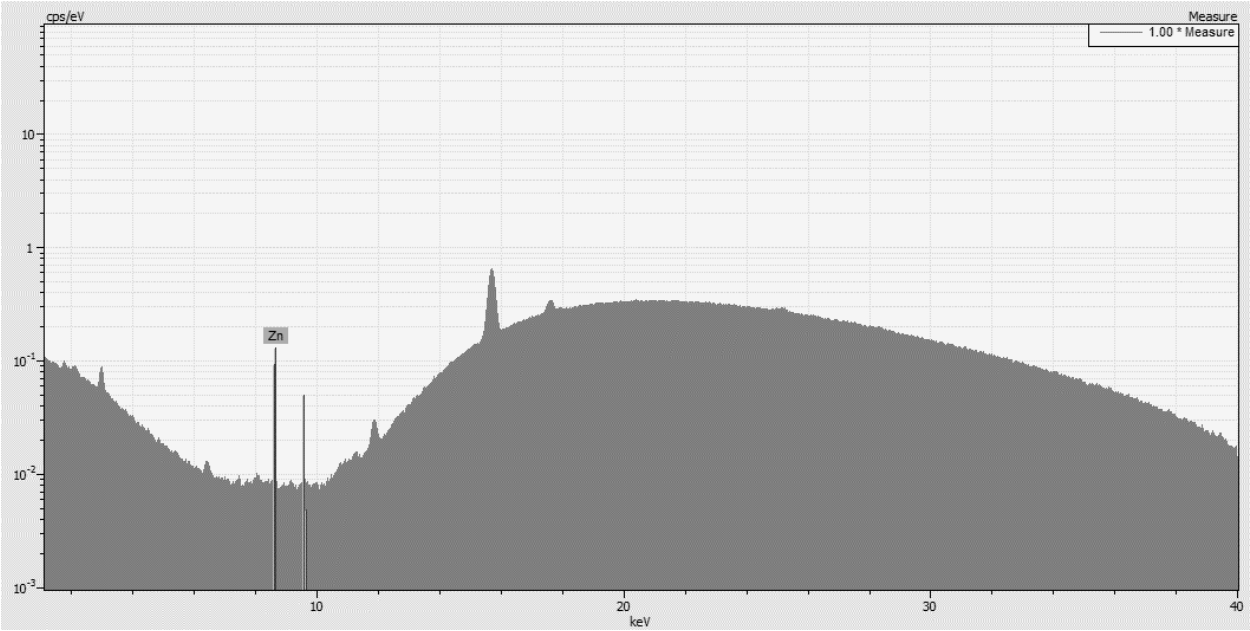

Figure S1 Detection of the zinc content in the test sample using X-Ray fluorescence.