Supplementary Material

for

Cobalt complexes bearing scorpionate ligands: synthesis, characterization, cytotoxicity and DNA cleavage

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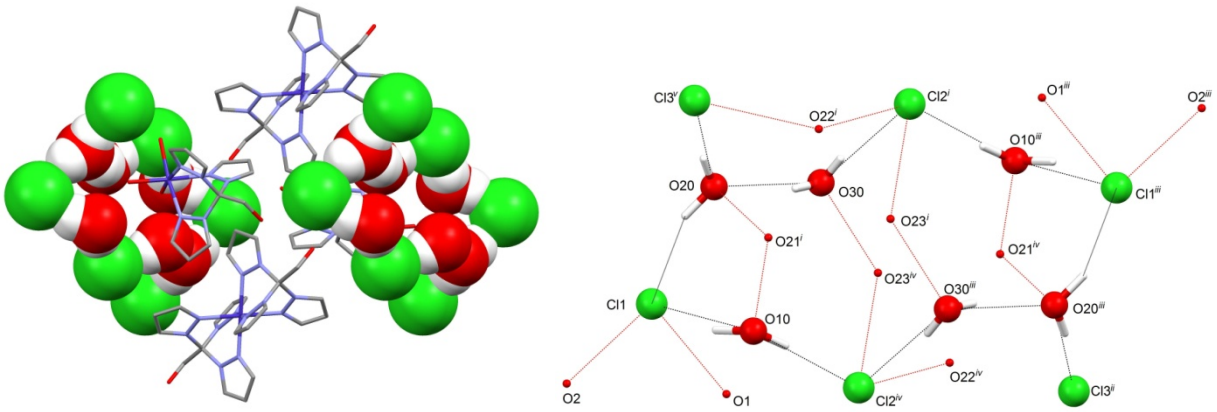
The scorpionate ligands in **1** and **3** coordinate in the *NNN* tridentate mode. The Co–N bond distances are in the 2.080(4) – 2.155(3) Å range with the largest values in **1**, what can result from a greater *trans* effect of sulfonate and methoxide groups as compared to the ligands in the other complexes.

In compound **1** medium intensity intermolecular π···π interaction involving the N1- and the N5-containing pyrazolyl rings (*centroid…centroid* distance of 3.644(2) Å), as well as several C-H···π interactions of reasonable intensity (from which the strongest example is C2–H2···N3-pyrazolyl 2.73 Å, 135º) could be found.



(a) **(b)**

Fig. S1 – a) Fragment of the crystal packing diagram of **3** in a view perpendicular to the *ac* plane showing the intercalation of cyclic $\{(H_2O)_6(Cl)_4(Cl)_2\}^{6-}$ clusters (represented by space filling models) into the metal-organic matrix (depicted as sticks). b) Perspective representation (arbitrary view) of hybrid water-chloride hydrogen-bonded assemblies and their connections to the metal-organic matrixes which were omitted for clarity. Hydrogen bonds involving just the water molecules and the chloride anions are represented as black dotted lines and those involving the metal complexes as dotted red lines. Symmetry operation to generate equivalent atoms: *i*) x,y,1+z; *ii*) 2-x,1-y,2-z; *iii*) 1-x,1-y,2-z ; *iv*) 1-x,1-y,1-z; *v*) -1+x,y,z.

Table S1 – Crystallographic data for compounds $[Co(OSO_3H)(OCH_3)(HOCH_3)\{HC(pz)_3\}]$ (**1**) and $[Co\{HOCH_2C(pz)_3\}_2].[Co\{HOCH_2C(pz)_3\}(H_2O)_3]_2(Cl)_6.6H_2O$ (**3**.$6H_2O$).

	1	**3**.$6H_2O$
Empirical formula	$C_{12}H_{18}CoN_6O_6S$	$C_{44}H_{72}Cl_6Co_3N_{24}O_{16}$
Formula weight	433.31	1582.75
Crystal system	Monoclinic	Triclinic
Space group	*P* 21/n	*P* -1
a (Å)	7.8225(6)	11.590(3)
b (Å)	12.4161(10)	11.736(2)
c (Å)	17.4883(15)	13.908(5)
α(°)	90	108.336(13)
β(°)	93.384(5)	105.474(13)
λ(°)	90	102.185(9)
V (Å^3)	1695.6(2)	1638.2(8)
Z	4	1
T (K)	150(2)	150(2)
Density (cal.) (Mg/m^3)	1.697	1.604
μ (mm^{-1})	1.180	1.077
F(000)	892	815
Rfl. collected / unique /obs	21091 / 3107 / 2649	14754 / 5842 /4331
R_{int}	0.0643	0.0407
R1[a] ($I \geq 2\sigma$)	0.0545	0.0541
*w*R2[b] ($I \geq 2\sigma$)	0.141	0.1466
Goodness-of-fit on F^2	1.033	1.038

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$

Table S2 – Selected bond distances (**Å**) and angles (°) for the cobalt compounds $[Co(OSO_3H)(OCH_3)(HOCH_3)\{HC(pz)_3\}]$ (**1**) and $[Co\{HOCH_2C(pz)_3\}_2].[Co\{HOCH_2C(pz)_3\}(H_2O)_3]_2(Cl)_6.6H_2O$ (**3**.$6H_2O$).

		1	**3**.$6H_2O$
Co–N			
	Shortest	2.135(3)	2.080(4)
	Longest	2.155(3)	2.117(4)
Co–O			
	Shortest	2.044(2)	2.044(4)
	Longest	2.110(3)	2.143(4)
Intermolecular Co···Co		6.733	7.894
∠ N–Co–N			
	Shortest	82.70(11)	82.99(17)
	Longest	84.56(11)	180.0(4)
∠ O–Co–N			
	Shortest	90.48(11)	90.57(17)
	Longest	175.79(11)	173.62(17)

Table S3. Hydrogen bond interactions [Å, °] in **3**.[a]

D–H···A	*d*(H···A)	*d*(D···A)	∠(D–H···A)
Within water-chloride cluster			
O10–H10A···Cl1 [i]	2.36(2)	3.216(4)	172(6)
O10–H10B···Cl2	2.31(4)	3.090(5)	150(6)
O20–H20A···Cl1	2.60(7)	3.384 (5)	153(6)
O20–H20B···Cl3[ii]	2.2092	3.099(5)	165.6(3)
O30–H30A···Cl2[iii]	2.3630	3.202(4)	168.5(3)
O30–H30B···O20[i]	2.039	2.798(6)	150
Between water-chloride network and metal-organic units			
O1–H1···Cl1[i]	2.52	3.113(4)	131.0
O2–H2···Cl1	2.69	3.198(4)	122.0
O21–H21A···O20[iv]	1.995	2.875(6)	150.9
O21–H21C···O10[iii]	1.762	2.630(6)	148.1(3)
O22–H22B···Cl3[v]	2.1698	3.127(4)	171.1(2)
O22–H22C···Cl2	2.3086	3.204(4)	154.0
O23–H23A···Cl2	2.3483	3.183(4)	153.0
O23–H23B···O30	1.704	2.640(5)	167.9(3)

[a] Symmetry codes: (i) 1-x,1-y,1-z; (ii) –x,1-y,1-z; (iii) 1-x,1-y,-z; (iv) x,y,-1+z; (v) –x,1-y,-z.

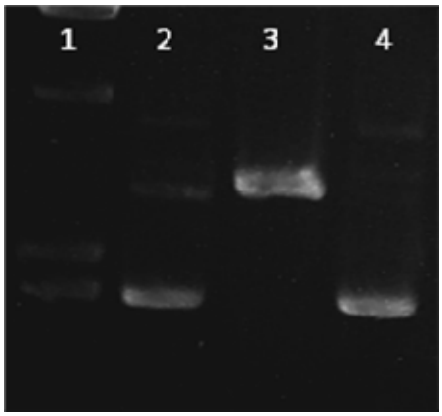


Fig. S2. Agarose gel electrophoresis (0.8% (w/v)) concerning the incubation of pBSKII plasmidic DNA (pDNA) at pH = 7.0 and 37 ◦C for 4 h with complex **3** or $CoCl_2$. Lane 1: Molecular ladder λDNA/HindIII; lane 2: pBSkII incubated in the presence of 50 μM of complex **3**; lane 3: linearized pBSkII; lane 4: pBSKII incubated in the presence of 50 μM of $CoCl_2$.

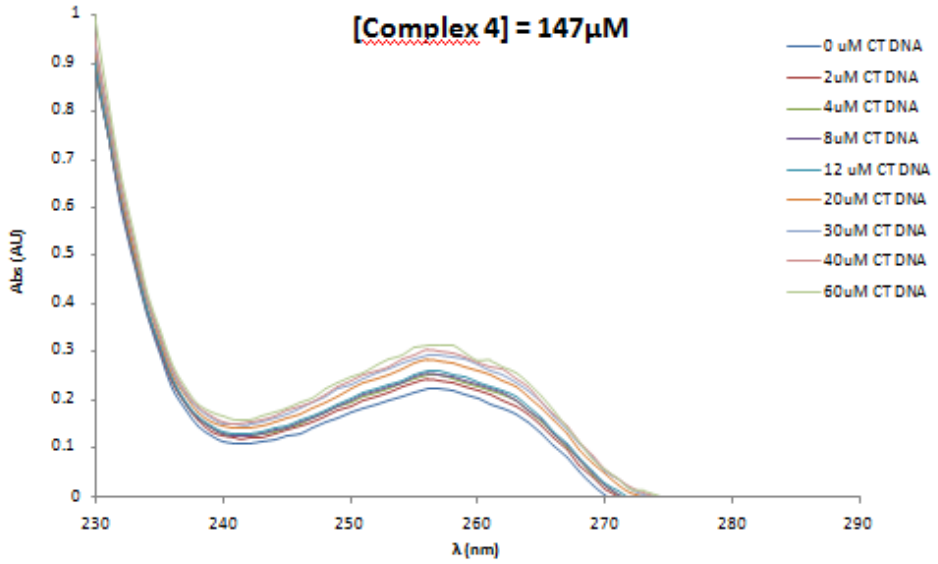


Fig. S3. UV-visible spectra of complex **4** in the presence of increasing concentrations of CT DNA.

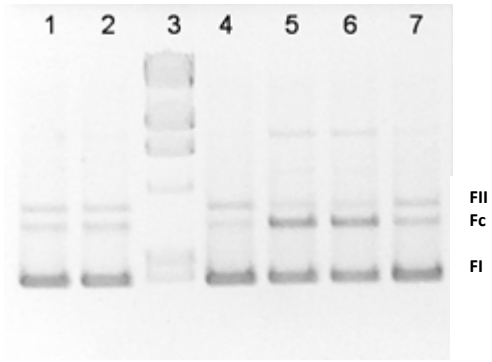


Fig. S4 - Agarose gel electrophoresis (0.8% (w/v)) of pDNA cleavage experiments in the presence of complex **3**. Lane 1: pBSKII incubated in the presence of 50 μM of complex **3** alone; lane 2: pBSKII incubated in the presence of 200 μM of H_2O_2 alone; lane 3: molecular ladder λDNA/HindIII; lane 4: pBSKII (control); lane 5: pBSKII incubated in the presence of 50 μM complex **3** and 200 μM H_2O_2; lane 6 – pBSKII incubated in the presence of 250 μM complex **3** and 200 μM H_2O_2; lane 7 – pBSKII incubated in the presence of 250 μM complex **3,** 200 μM H_2O_2 and DMSO (3% v/v). FI –supercoiled isoform of DNA; Fc – linear isoform of DNA (double strand breaks); FII- relaxed (nicked) isoform of DNA.