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Supplementary Materials

Copper(II) Prevents the Saccarine-Dialkylcyanamide Coupling Forming Mononuclear (Saccharinate)(Dialkylcyanamide)copper(II) Complexes

Yulia N. Toikka, Dar'ya V. Spiridonova, Alexander S. Novikov and Nadezhda A. Bokach *

Institute of Chemistry, Saint Petersburg State University, 7/9 Universitetskaya Nab., 199034 Saint Petersburg, Russia; helmi24@mail.ru (Y.N.T.); spiridonovadarya@mail.ru (D.V.S.); ja2-88@mail.ru (A.S.N.)
* Correspondence: n.bokach@spbu.ru

Crystal data and structure refinement

Table S1. Crystal data and structure refinement for **1**, **1**·2H_2O, **3**·2THF, and [Cu(sac)$_2$(H_2O)$_4$]·2H_2O.

Sample	**1**	**1**·2H_2O	**3**·2THF	[Cu(sac)$_2$(H_2O)$_4$]·2H_2O
Identification code	YN44	YN45	15501_YN-56	16953_YN-132
Empirical formula	$C_{17}H_{18}CuN_4O_8S_2$	$C_{17}H_{22}CuN_4O_{10}S_2$	$C_{22}H_{24}CuN_2O_8S_2$	$C_{14}H_{20}CuN_2O_{12}S_2$
Formula weight	534.01	570.04	572.09	535.98
Temperature/K	100(2)	100(2)	100(2)	100(2)
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	Pnma	$Cmc2_1$	I2/a	$P2_1/c$
a/Å	7.14100(10)	23.4161(3)	11.51090(10)	8.32260(10)
b/Å	23.8599(4)	13.29850(10)	21.0713(2)	16.3127(2)
c/Å	12.48922(19)	7.23910(10)	20.3473(3)	7.22800(10)
α/°	90	90	90	90
β/°	90	90	98.7190(10)	100.9120(10)
γ/°	90	90	90	90
Volume/Å^3	2127.96(6)	2254.25(5)	4878.20(10)	963.56(2)
Z	4	4	8	2
ρ_{calc}g/cm^3	1.667	1.680	1.558	1.847
μ/mm^{-1}	3.773	3.670	3.310	4.292
F(000)	1092.0	1172.0	2360.0	550.0
Crystal size/mm^3	0.18 × 0.16 × 0.1	0.1 × 0.08 × 0.06	0.08 × 0.07 × 0.04	0.24 × 0.2 × 0.12
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.41 to 139.888	7.55 to 134.982	6.074 to 139.988	10.826 to 154.428
Index ranges	$-8 \le h \le 6$, $-29 \le k \le 27$, $-15 \le l \le 15$	$-28 \le h \le 27$, $-12 \le k \le 15$, $-8 \le l \le 8$	$-14 \le h \le 14$, $-25 \le k \le 25$, $-24 \le l \le 24$	$-10 \le h \le 10$, $-20 \le k \le 20$, $-7 \le l \le 9$
Reflections collected	7905	8503	32341	14210
Independent reflections	2068 [R_{int} = 0.0314, R_{sigma} = 0.0247]	1940 [R_{int} = 0.0470, R_{sigma} = 0.0376]	4625 [R_{int} = 0.0322, R_{sigma} = 0.0203]	2023 [R_{int} = 0.0307, R_{sigma} = 0.0153]
Data/restraints/parameters	2068/0/163	1940/1/175	4625/0/318	2023/0/183
Goodness-of-fit on F^2	1.050	1.031	1.060	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0929	R_1 = 0.0321, wR_2 = 0.0821	R_1 = 0.0296, wR_2 = 0.0851	R_1 = 0.0254, wR_2 = 0.0706
Final R indexes [all data]	R_1 = 0.0357, wR_2 = 0.0951	R_1 = 0.0322, wR_2 = 0.0822	R_1 = 0.0309, wR_2 = 0.0861	R_1 = 0.0256, wR_2 = 0.0707
Largest diff. peak/hole / e Å^{-3}	0.56/−0.46	0.50/−0.56	0.78/−0.62	0.42/−0.44
Flack parameter		−0.01(3)		
CCDC number	2062446	2062447	2062448	2062451

Experimental spectra and TG/dTG curves

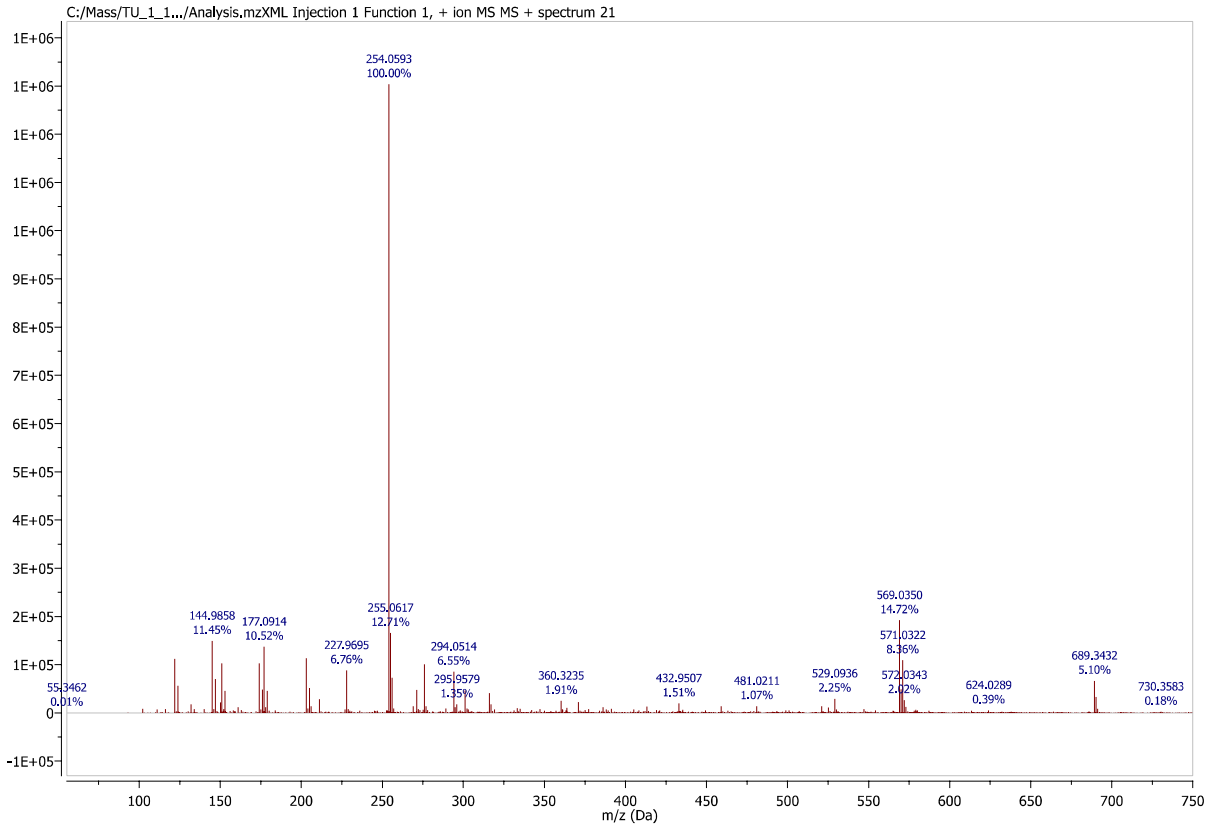

Figure S1. HRESI$^+$-MS spectrum of the reaction mixture $CuCl_2$/$NCNMe_2$/SacNa in MeCN. The peak at m/z 254.0593 corresponds to 1:1 addition product of SacH to $NCNMe_2$ (m/z calcd for $[M+H]^+$ 254.0599).

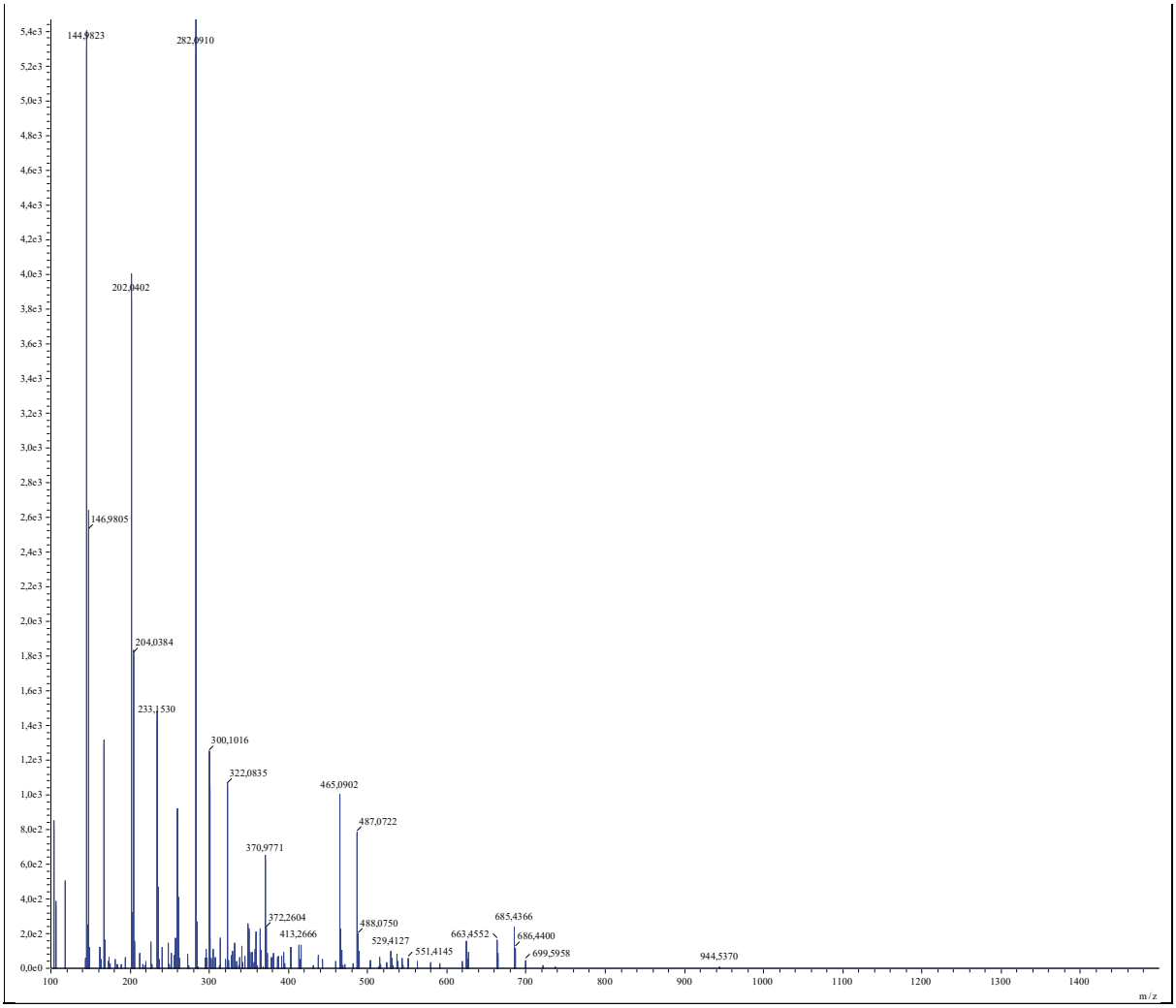

Figure S2. HRESI$^+$-MS spectrum of the reaction mixture $CuCl_2$/$NCNEt_2$/SacNa in MeCN. The peak at m/z 282.0910 corresponds to 1:1 addition product of SacH to $NCNEt_2$ (m/z calcd for $[M+H]^+$ 282.0913).

Electrospray ionization mass-spectra were obtained on a Bruker micrOTOF and Shimadzu LCMS-9030 spectrometers equipped with an electrospray ionization (ESI) source. The instruments were operated in positive ion mode using a *m*/*z* range 50–3000.

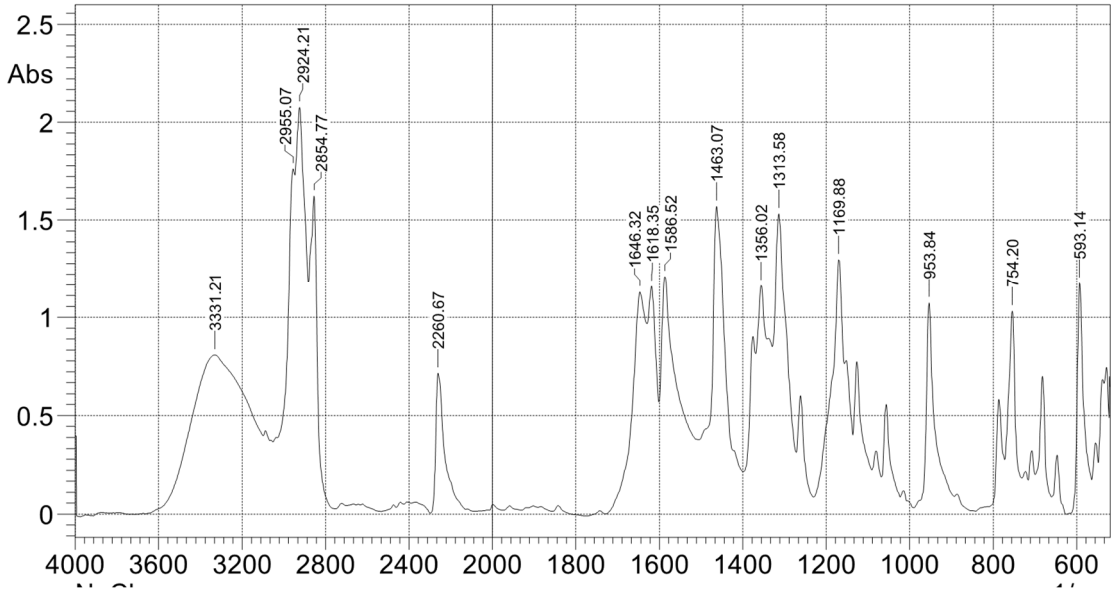

Figure S3. IR spectrum of **1** in Nujol.

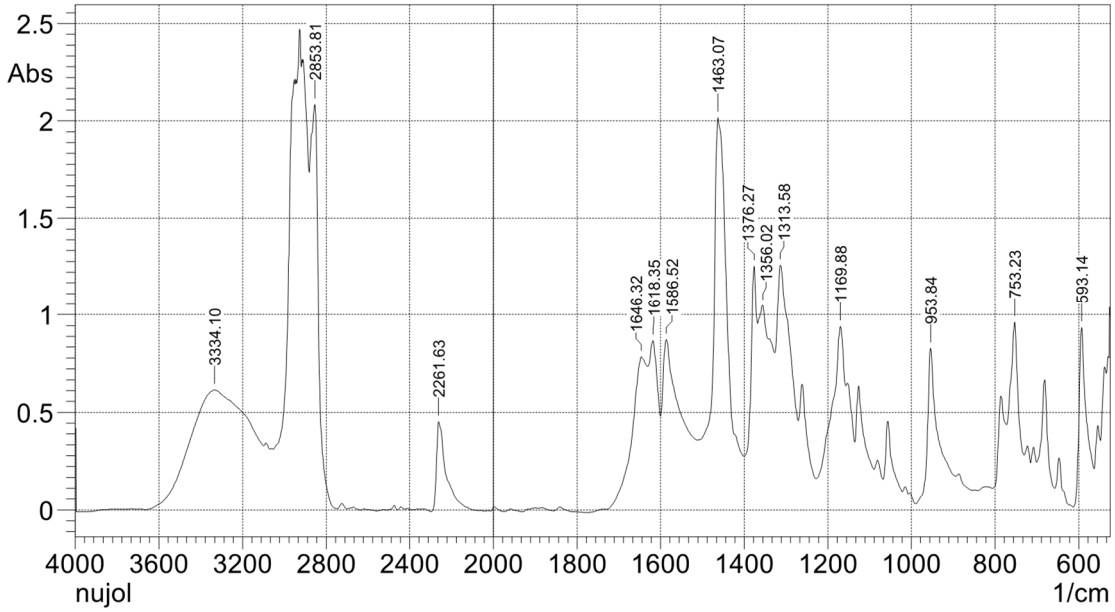

Figure S4. IR spectrum of **1**·2H_2O in Nujol.

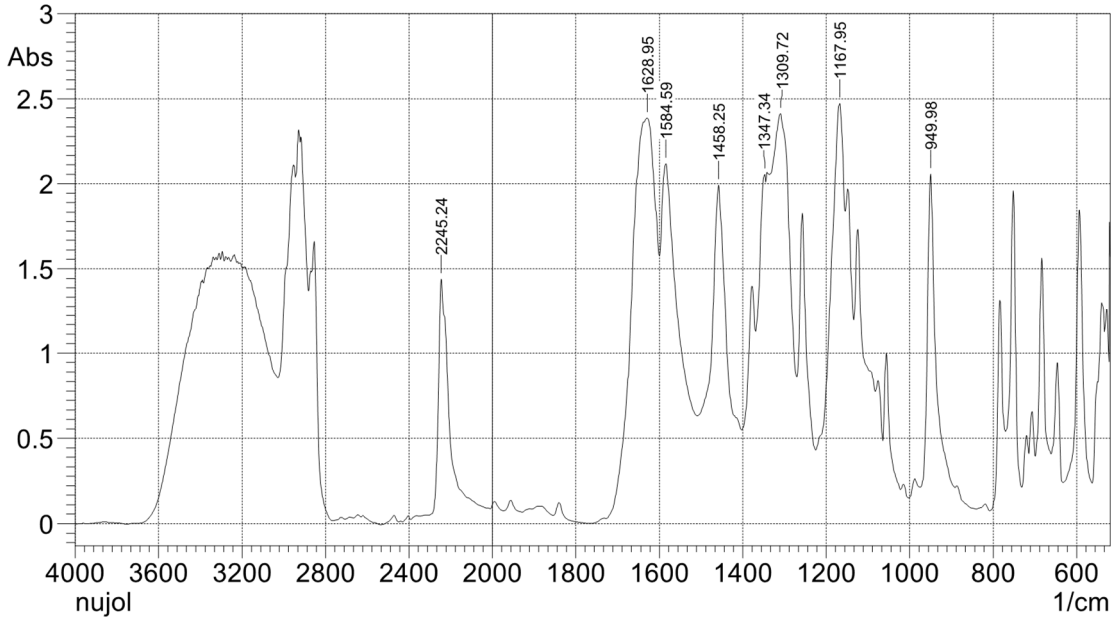

Figure S5. IR spectrum of **2** in Nujol.

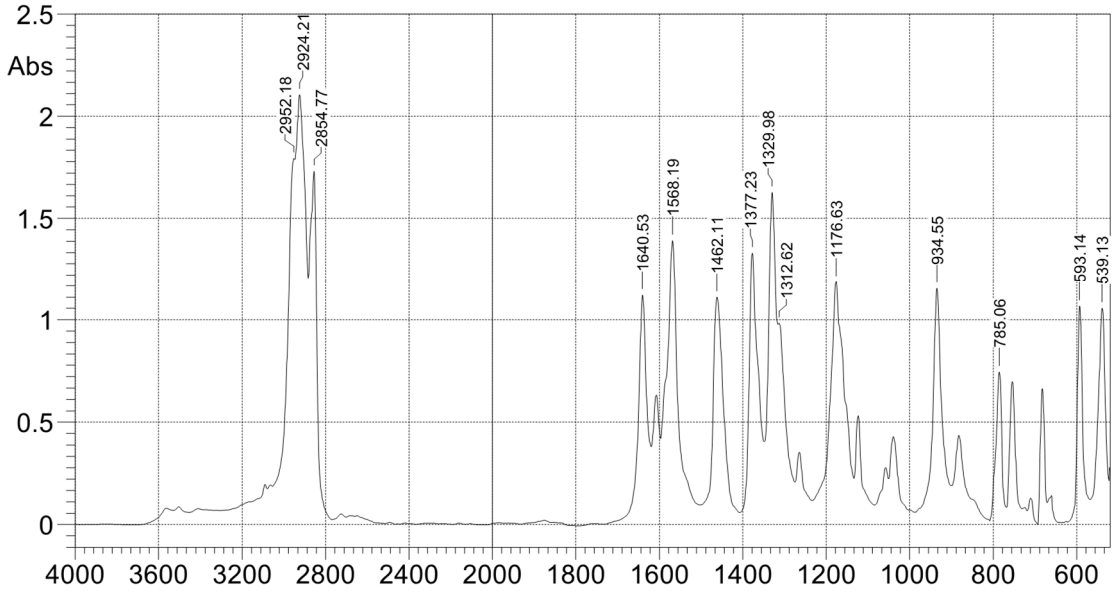

Figure S6. IR spectrum of **3**·2THF in Nujol.

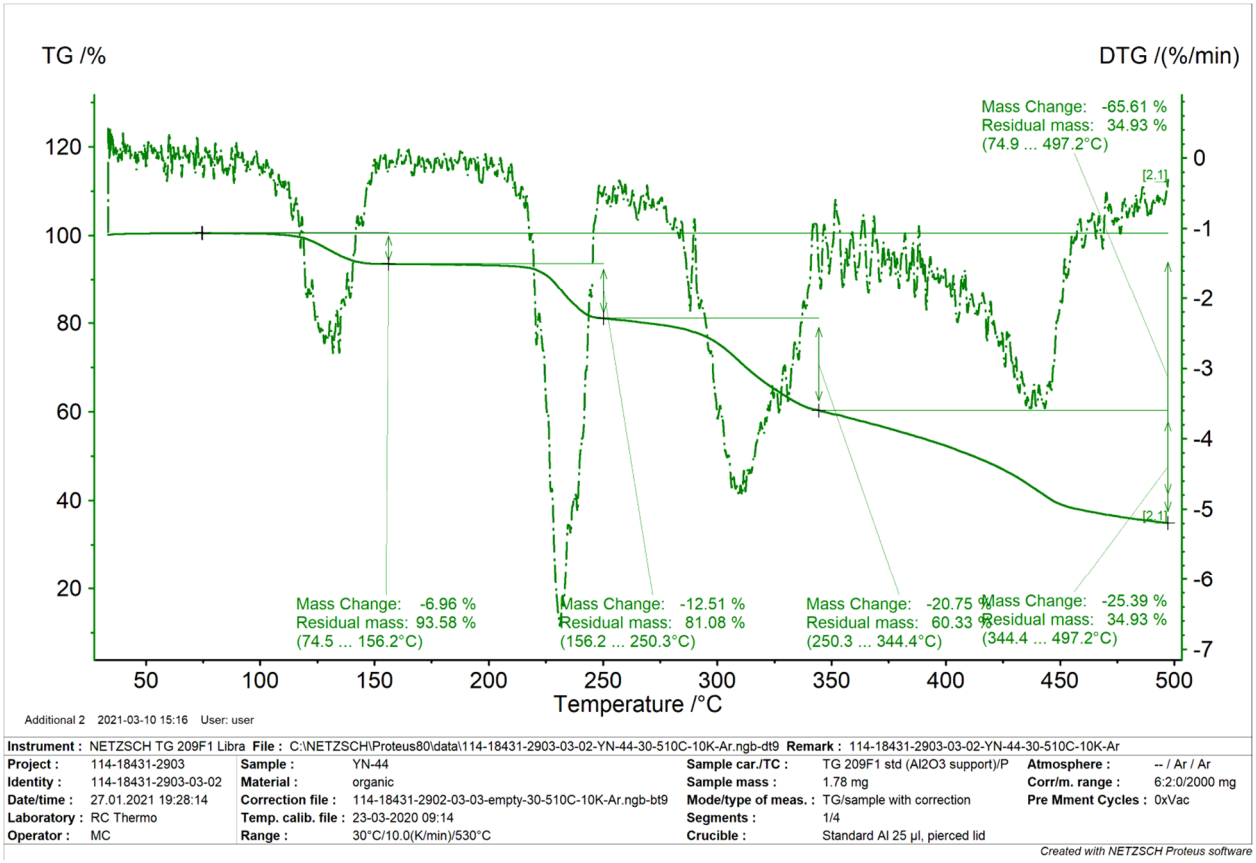

Figure S7. TG and dTG curves for **1**.

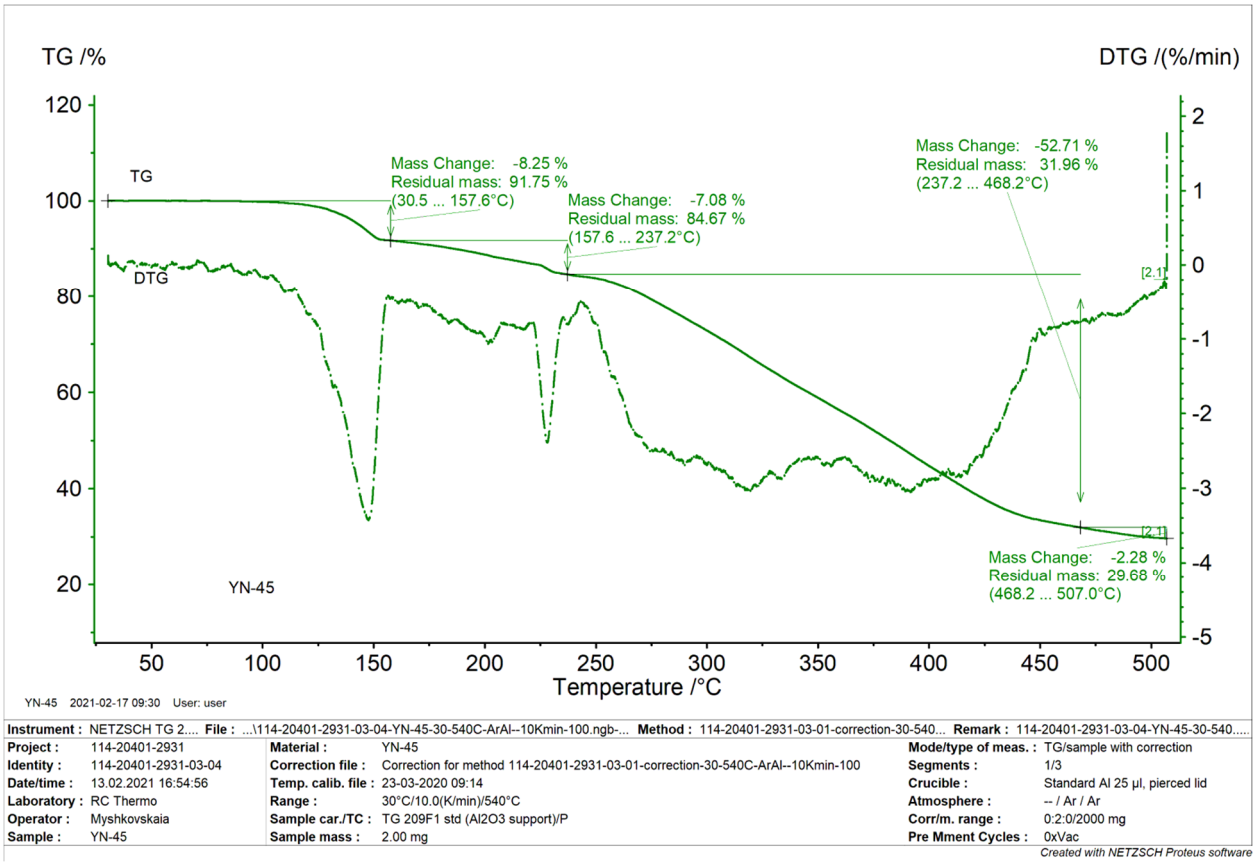

Figure S8. TG and dTG curves for **1**·2H_2O.

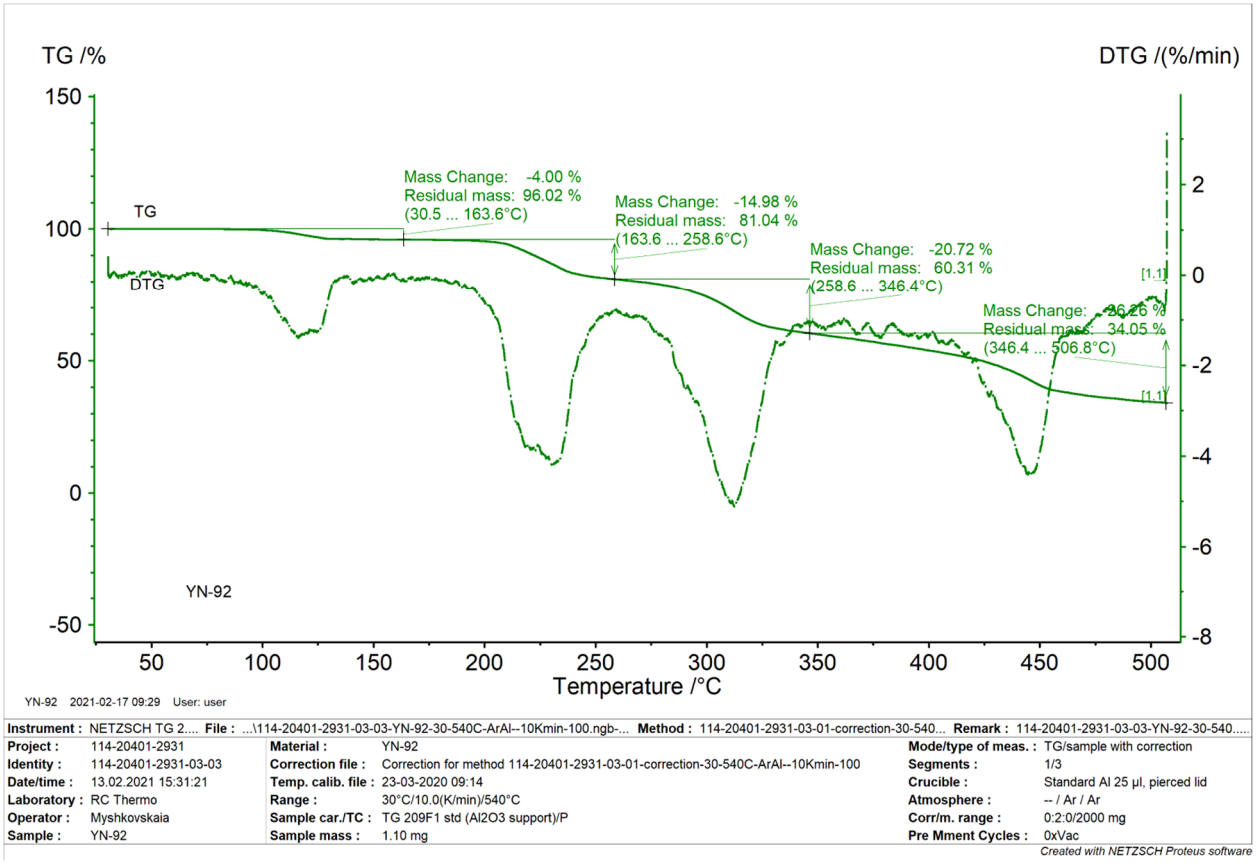

Figure S9. TG and dTG curves for **2**.

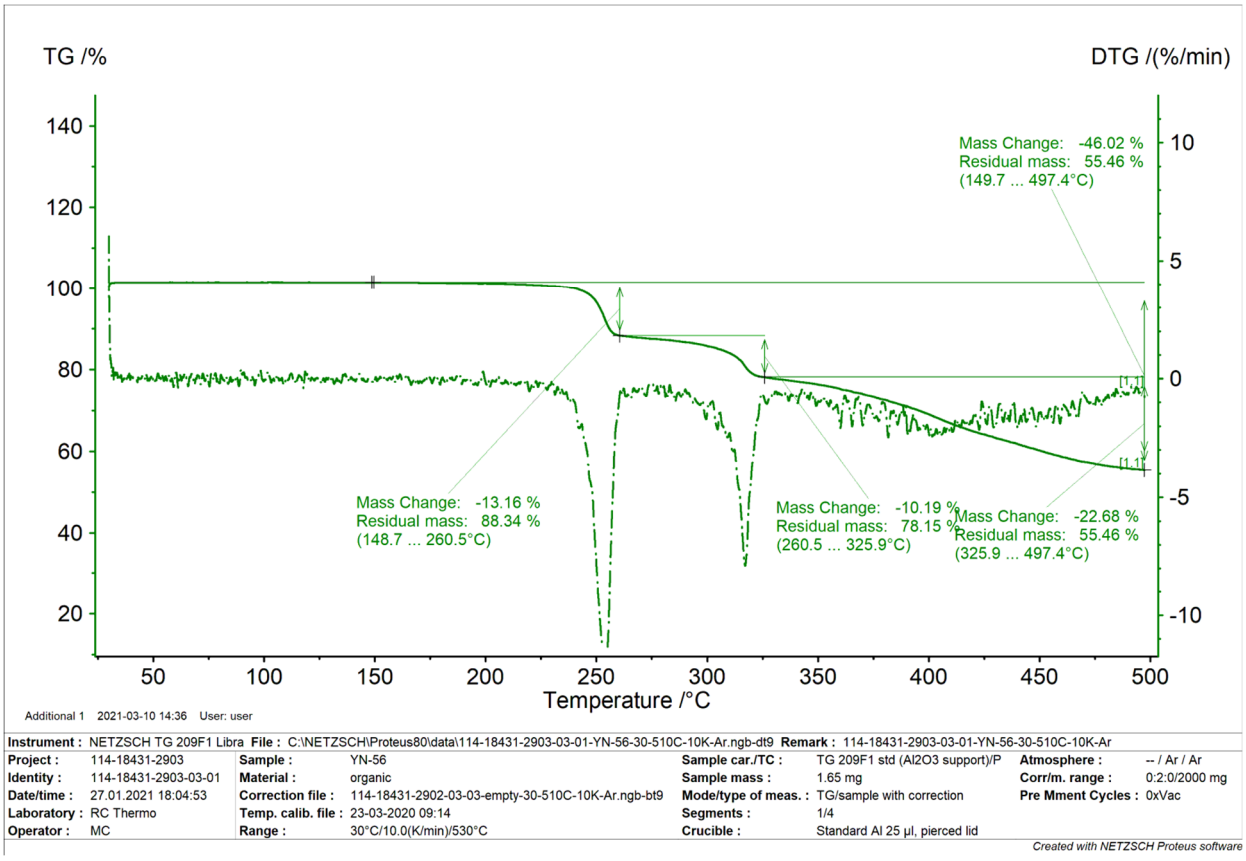

Figure S10. TG and dTG curves for **3**·2THF.

Synthesis and characterization of [Cu(sac)$_2$(H$_2$O)$_4$]

Synthesis of [Cu(sac)$_2$(H$_2$O)$_4$]. $CuCl_2 \cdot 2H_2O$ (0.25 mmol) were dissolved in any of the following solvents – MeOH, EtOH, or MeCN (2 mL) at RT, whereupon a solution of sodium saccharinat (0.25 mmol) and $NCNC_5H_{10}$ in MeOH, EtOH, or MeCN (2 mL) was added. The resulting mixture was left to stand for 3–5 days at RT without stirring and the pale blue prismatic crystals were precipitated; these crystals were washed by methanol and dried in air at RT. The isolated yields are 20–30%. IR in KBr (selected bands, cm^{-1}): 33566 m, 3504 m, and 3414 m, ν(O–H), 3097 m-s br ν(C–H and O–H), 1619 s brand 1580 m ν(C=O) and δ(O–H), 1306 m-s ν_{sym} (S=O), 1165 m-s ν_{asym} (S=O).

Complex $[Cu(sac)_2(H_2O)_4] \cdot 2H_2O$ contains copper(II) center in distorted octahedral environment. The Cu–N distance (2.0595(13) Å) is slightly longer that those in **1** and $\mathbf{1} \cdot 2H_2O$. Two Cu–O bonds exhibit different distances (1.9591(13) and 2.4579(16) Å) due to Jahn-Teller effect. Coordinated and solvated molecules of H_2O are involved in formation of system of HB. One of H_2O ligand form intramolecular HB with C=O group of sac^- ligand and participates in HB with solvated H_2O as HB donor. Other coordinated H_2O forms intermolecular HB with O=S group of neighbor molecule of $[Cu(sac)_2(H_2O)_4] \cdot 2H_2O$ and acts as a HB acceptor toward solvated H_2O. In turn, solvated H_2O acts as HB donor toward O=C group of sac^- ligand and one H_2O ligand, and is HB acceptor toward another H_2O ligand. This system of HB lead to formation of wavy two-dimensional layers in the structure of $[Cu(sac)_2(H_2O)_4] \cdot 2H_2O$.

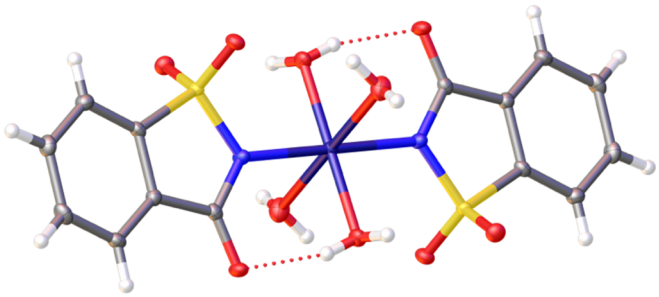

Figure S11. Molecular structure of $[Cu(sac)_2(H_2O)_4] \cdot 2H_2O$ with the atomic numbering. Thermal ellipsoids are given at the 50% probability level. H_2O hydrated molecules are omitted for clarity.

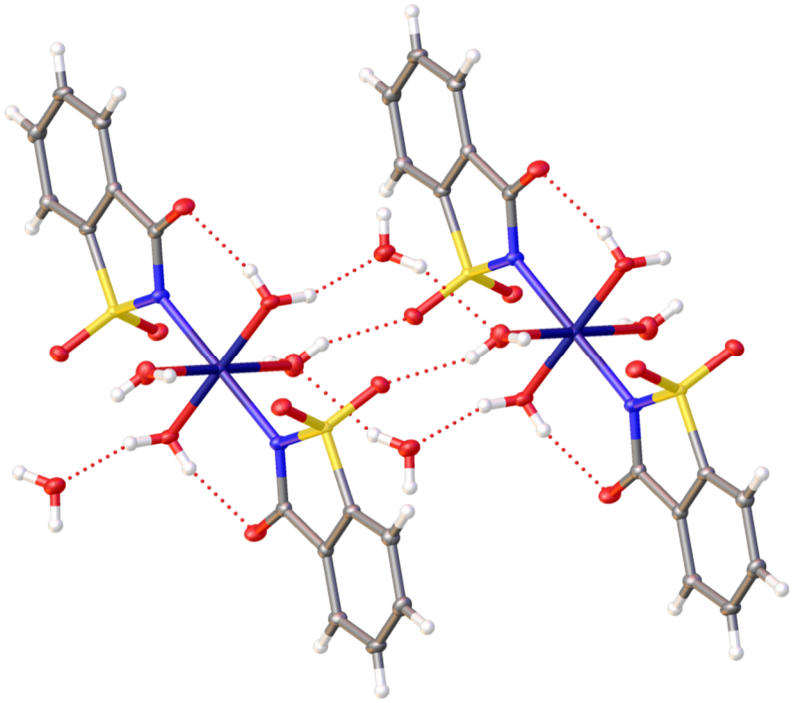

Figure S12. A fragment of crystal packing of $[Cu(sac)_2(H_2O)_4]\cdot 2H_2O$ with the intra- and intermolecular HBs shown in dotted lines.

Cartesian atomic coordinates

Table S2. Cartesian atomic coordinates for optimized equilibrium model structure **1**.

Atom	X	Y	Z
S	−2.880281	0.851824	−0.068370
O	−2.264106	−2.792854	0.436240
O	−2.351861	1.473455	−1.277469
O	−3.080701	1.708401	1.095877
N	−1.980442	−0.516669	0.309790
C	−2.714480	−1.652683	0.242877
C	−4.128640	−1.399826	−0.140831
C	−5.137836	−2.337644	−0.292505
H	−4.934317	−3.388688	−0.098613
C	−6.392114	−1.886617	−0.695335
H	−7.204303	−2.599138	−0.824165
C	−6.624144	−0.531720	−0.939136
H	−7.613184	−0.205901	−1.255079
C	−5.608581	0.411958	−0.785226
H	−5.780602	1.469994	−0.971396
C	−4.372027	−0.060479	−0.390369
N	0.004770	1.373185	1.087906
N	−0.015047	3.734620	0.367895
C	−0.006176	2.479200	0.707927
C	−1.285262	4.380844	0.039491
H	−1.455036	4.362665	−1.044719
H	−1.244667	5.417365	0.393521
H	−2.101741	3.851104	0.538719
C	1.225949	4.367746	−0.076976
H	1.262746	4.403201	−1.173382
H	1.261148	5.385256	0.329230

H	2.079577	3.791367	0.291276
O	0.007540	−2.114629	−0.992638
H	−0.770788	−2.631260	−0.692622
H	0.785922	−2.629360	−0.690156
Cu	0.002796	−0.507518	0.429690
O	0.002974	−2.070459	1.993769
H	−0.777653	−2.582447	1.698104
H	0.787115	−2.579032	1.701190
S	2.878579	0.857878	−0.081978
O	2.278580	−2.785332	0.449540
O	2.342715	1.462514	−1.296589
O	3.077063	1.731579	1.069686
N	1.986525	−0.510889	0.312284
C	2.724783	−1.644492	0.250931
C	4.138266	−1.387892	−0.132864
C	5.153184	−2.321487	−0.271710
H	4.954442	−3.371824	−0.069210
C	6.407080	−1.867070	−0.671916
H	7.223938	−2.576073	−0.790134
C	6.633242	−0.512966	−0.925444
H	7.622407	−0.184262	−1.237975
C	5.611769	0.426415	−0.784933
H	5.779430	1.483975	−0.977705
C	4.375559	−0.049501	−0.393112