Electronic Supplementary Material (ESI) for Dalton Transactions.

Solvent effects on the crystal structure of silver pentacyanocyclopentadienide: supramolecular isomerisms and solvent coordination

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SUPPORTING INFORMATION

compound	**1**	**2**	**3**
Temperature (K)	298	253	100
Empirical formula	C_{10} Ag N_5	C_{20} Ag_2 N_{10}	C_{12} H_3 Ag N_6
M	298.02	596.04	339.07
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P 2_1/n	P 2_1 2_1 2	C 2/c
Crystal size (mm)	0.15 x 0.13 x 0.12	1.000 x 0.250 x 0.250	0.09 x 0.07 x 0.02
a (Å)	a = 6.8270(10)	13.726(13)	36.9518(10)
b (Å)	b = 11.5780(10)	18.821(10)	3.83030(10)
c (Å)	c = 12.151(2)	11.243(9)	20.8394(6)
ß [°]	98.450(10)	90	119.6870(10)
V [Å3]	950.0(2)	2904(4)	2562.39(12)
Z	4	4	8
Dc [g/dm3]	2.084	1.363	1.758
F (000)	568	1136	1312
μ (MoKα) [mm-1]	2.094	1.370	1.566
Absorption Correction	Psi-Scan	Sphere	Semi-empirical from equivalents
Tmax/ Tmin	0.34 and 0.31	0.3747 and 0.3643	0.7457 and 0.6351
no. of total reflections	3717	5703	13444
Data / parameters	2775 / 145	5128 / 289	3183 / 173
Absolute structure Parameter		-0.008(19)	
R1 [I>2σ(I)]	0.0655	0.0305	0.0250
wR2 (all data)	0.1200	0.0839	0.0753
GOOF	1.003	1.022	1.107
Largest diff. peak and hole [e Å-3]	1.108 and -1.288	0.514 and -1.005	0.562 and -0.979
CCDC-#	1833878	1833879	1833877

Table SI1: Experimental details for the crystal structure determinations.

Details of the crystallization procedures:

Compd 1: CuBr (72 mg, 0.5 mmol)) and $Ag[C_5(CN)_5]$ (149 mg, 0.5 mmol) were mixed as solids and suspended in MeOH (15 mL). The suspension was heated to 60°C for 3 h. A light yellow precipitate formed under a faint yellow-green solution. After cooling to r.t., the solution was siphoned off from the precipitate and filtered. Leaving the solution on air at r.t. produced yellow needles, which were used for the crystal structure determination. Elemental analysis (found: C 40.12, N 22.54, H 0.63%) showed that the crystals were not the expected Cu(I) complex (calcd C 47.35, N 27.61, H 0.0). Apparently the crystals were covered with some MeOH solvent (approx. 0.4 MeOH per formula unit).

(Repeated recrystallization of $Ag[C_5(CN)_5]$ from methanol finally yielded some crystals, which were used for re-determination of the cell parameters at room temperature (298 K) and at 143K. The found parameters (298K: a= 6.83Å, b= 11.58Å, c= 12.15Å, ß= 98.46°; 143K: 6.83Å/ 11.58Å/ 12.03Å/ 98.42°) confirmed the proposed identity of compound **1**)

Compd 2: Crude $Ag[C_5(CN)_5]$ (250 mg) was suspended in EtOH (25 mL) and heated to reflux for 3 h. After filtering the hot solution, the filtrate was collected in an Erlenmeyer flask and left at r.t. for several days. Thick yellow needles formed. When taken out of the mother liquor they turned quickly opaque. Therefore a crystal was taken out of the cooled crystallization mixture, mounted on top of a glass fibre using some silicone grease and measured at -20°C on the diffractometer.

Compd 3: MeCN (2 mL) was added to crude $Ag[C_5(CN)_5]$ (200 mg) in an Erlenmeyer flask, and the solid was dissolved via sonication. The solution was cooled to 5 °C and diluted with small amounts of toluene until a precipitate began to form. The mixture was filtered and then warmed to r.t.. The filtrate was subjected to slow vapor diffusion in a 5 mL round bottom flask at r.t. for several days until colorless platelets started to form.

*Further details for the structure determination of compd. **3**: A total of 688 frames were collected. The total exposure time was 1.04 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 21385 reflections to a maximum ϑ angle of 28.32° (0.75 Å resolution). The final cell constants of a = 36.9518(10) Å, b = 3.83028(10) Å, c = 20.8394(6)Å, ß = 119.6870(8)°, volume = 2562.38(19) Å^3, are based upon the refinement of the XYZ-centroids of 9987 reflections above 20 σ(I) with 6.165° < 2ϑ < 56.71°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.852.*

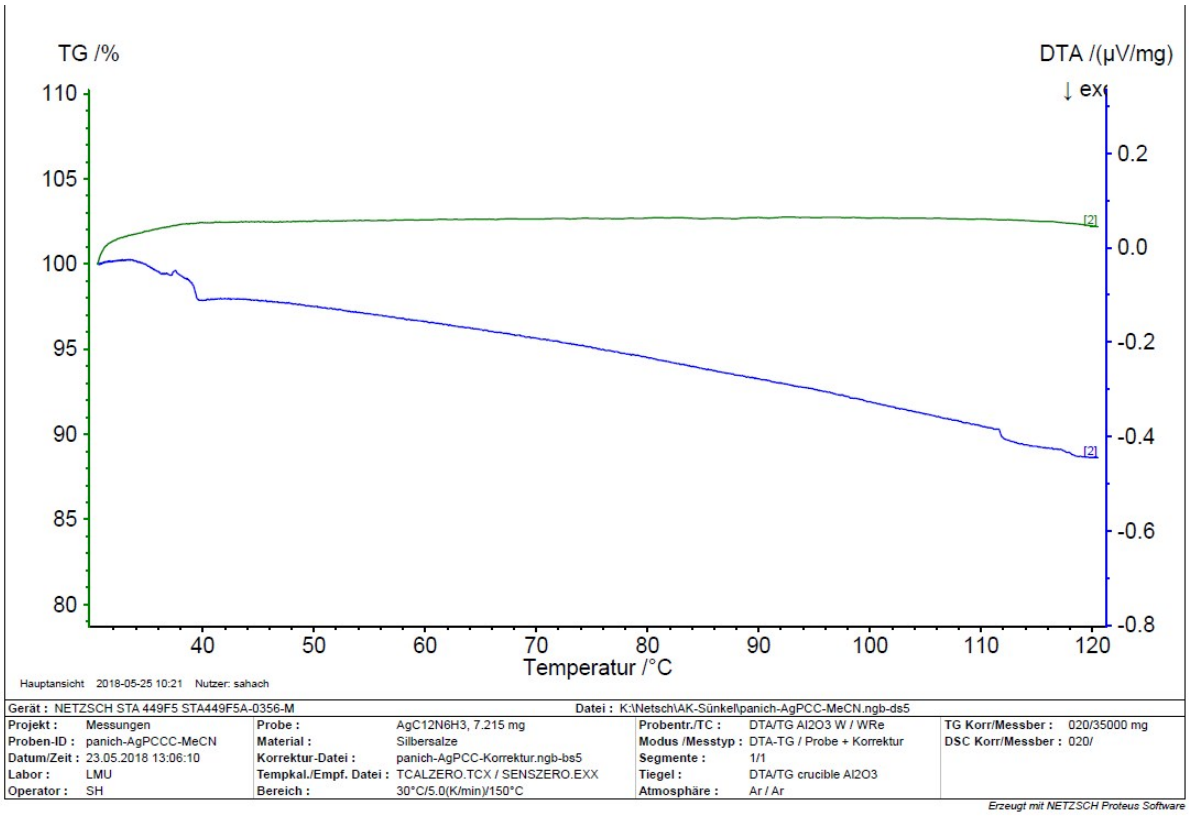

Figure SI_1: TG and TGA of compound **3**

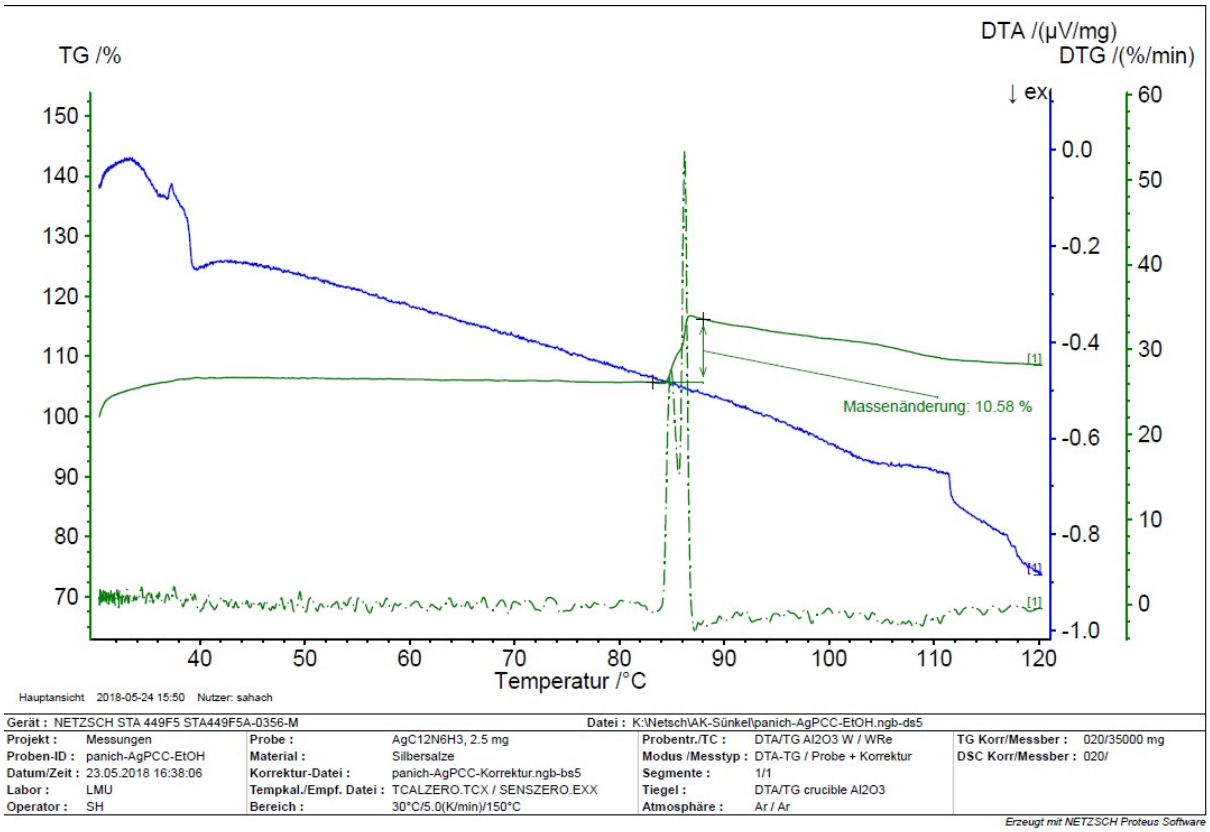

Figure SI_2: TG, DTA and DTG for compound **2**

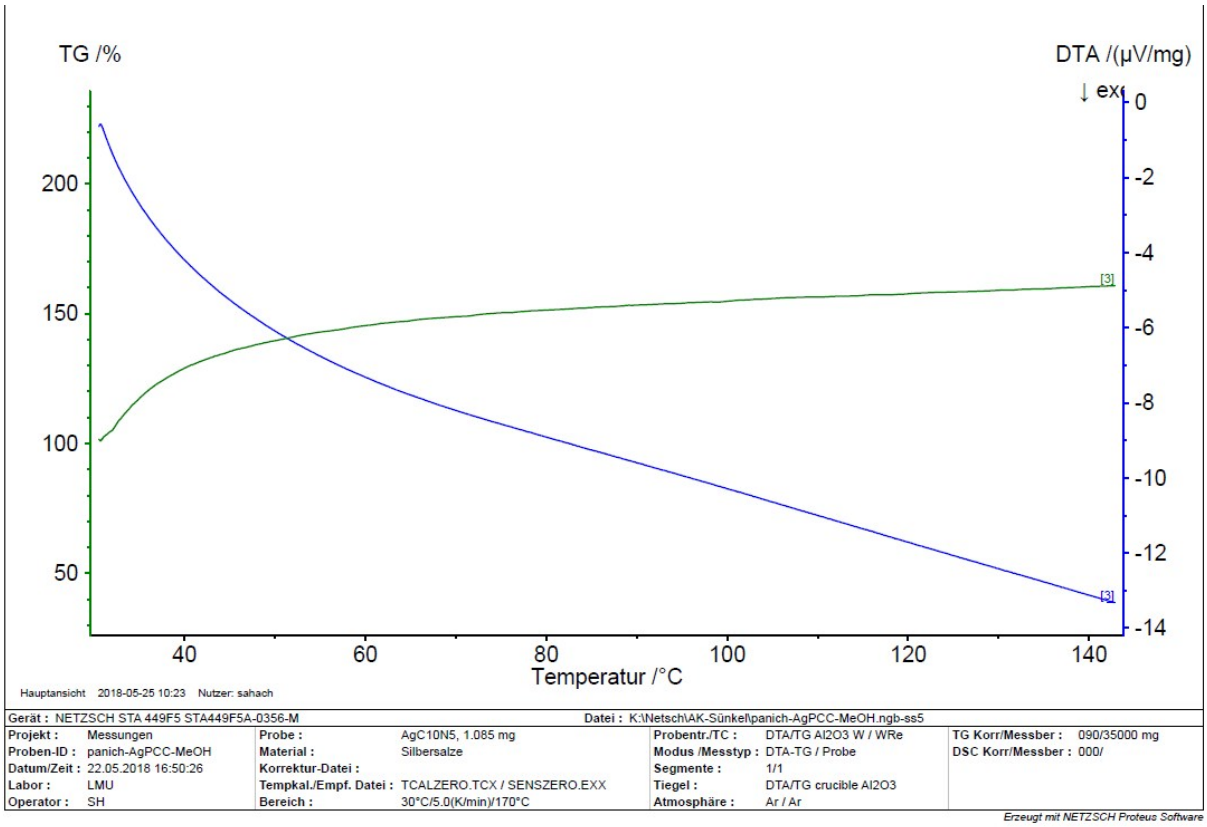

Figure SI_3: TG and DTA of compound **1** (uncorrected for heating effects)