SUPPLEMENTARY MATERIALS

Novel tetrahedral cobalt(II) silanethiolates: structures and magnetism

Daria Kowalkowska-Zedler,[a] Natalia Nedelko,[b] Katarzyna Kazimierczuk,[a] Pavlo Aleshkevych,[b] Renata Łyszczek,[c] Anna Ślawska-Waniewska,[b]* Agnieszka Pladzyk [a]*

[a] *Department of Inorganic Chemistry, Chemical Faculty, Gdańsk University of Technology, Narutowicza Str. 11/12, 80-233 Gdańsk, Poland*
[b] *Institute of Physics, Polish Academy of Sciences, Aleja Lotników 32/46, 02-668 Warsaw, Poland*
[c] *Department of Coordination and General Chemistry and Crystallography, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Skłodowska University in Lublin, M.C. Skłodowska Sq. 2, 20-031 Lublin, Poland*

* To whom correspondence should be addressed.
Email: agnieszka.pladzyk@pg.edu.pl

Supplementary Index

1. STRUCTURAL DATA

Table S1. Crystallographic data and structure refinement results for complexes **1**-**3**.

Complexes	**1**	**2**	**3**
Empirical formula	$C_{34}H_{76}CoN_2O_6S_2Si_2$	$C_{60}H_{136}Co_2N_8O_{12}S_4Si_4$	$C_{34}H_{70}CoN_4O_6S_2Si_2$
M_r (g mol^{-1})	788.19	1520.22	810.17
T (K)	120(2)	120(2)	120(2)
Wavelength (Å)	0.71073 (Mo K_α)	0.71073 (Mo K_α)	0.71073 (Mo K_α)
Crystal system	monoclinic	triclinic	monoclinic
Space group	*I*2/*a*	*P*-1	*C*2/*c*
a (Å)	33.4655(11)	10.4910(7)	16.320(4)
b (Å)	10.0373(2)	14.8839(10)	9.3357(17)
c (Å)	27.9753(8)	15.4659(10)	28.884(8)
α (°)	90	115.059(5)	90
β (°)	107.496(3)	90.642(5)	94.68(2)
γ (°)	90	94.524(6)	90
V (Å^3)	8962.3(5)	2178.1(3)	4386.1(19)
Z	8	1	4
Crystal size (mm)	0.51x0.28x0.22	0.28x0.13x0.10	0.33x0.10x0.08
D_{calc} (Mg m^{-3})	1.168	1.159	1.227
θ range (°)	2.504-25.242	2.49-25.499	2.504-25.499
Reflections collected/unique	32937 / 8322	15922 / 8003	16424 / 13044
R_{int}	0.0222	0.0712	.....
μ (mm^{-1})	0.568	0.584	0.584
Data/restraints/parameters	8322/0/442	8003/0/427	13044 / 0 / 233
Goodness of fit (GOF) on F^2	1.060	1.048	1.118
R_1, wR_2 [I>2σ(I)]	0.0258, 0.0659	0.0558, 0.1428	0.0781, 0.2245
R_1, wR_2 (all data)	0.0284, 0.0685	0.1025, 0.2017	0.0967, 0.2378
Largest diff. peak and hole (eÅ^{-3})	0.382 and -0.276	0.563 and -0.517	0.554 and – 0.538
CCDC number	2010158	2010156	2010160

Table S2. Selected bond lengths [Å] and angles [˚] for complexes **1**-**3**

	1	**2**	**3**
Bond lengths			
Co(1)-N(1)	2.0772(11)	2.043(4)	2.018(6)
Co(1)-N(2)	2.0672(11)	2.072(4)	
Co(1)-S(1)	2.3109(4)	2.2900(14)	2.341(2)
Co(1)-S(2)	2.3033(4)	2.3115(13)	
Si(1)-S(1)	2.0834(5)	2.0761(17)	2.080(3)
Si(2)-S(2)	2.0816(5)	2.074(2)	
Si(1)-O(1)	1.6314(10)	1.629(4)	1.636(5)
Si(1)-O(2)	1.6498(10)	1.627(4)	1.645(5)
Si(1)-O(3)	1.6291(10)	1.621(3)	1.626(5)
Si(2)-O(4)	1.6329(10)	1.634(4)	
Si(2)-O(5)	1.6304(10)	1.614(4)	
Si(2)-O(6)	1.6352(10)	1.641(4)	

	1	2	3
Bond angles			
N(1)-Co(1)-N(1)$^{\#}$			125.3(3)
N(1)-Co(1)-N(2)	116.85(4)	106.45(17)	
N(1)-Co(1)-S(1)	101.22(3)	109.91(13)	104.37(18)
N'(1)-Co(1)-S(1)			106,37(18)
N(1)-Co(1)-S(1)'			106,37(18)
N'(1)-Co(1)-S(1)'			104.37(18)
N(1)-Co(1)-S(2)	99.22(3)	106.89(13)	
N(2)-Co(1)-S(1)	110.13(1)	111.04(12)	
N(2)-Co(1)-S(2)	101.95(3)	102.31(11)	
S(1)-Co(1)-S(1)$^{\#}$			109.57(10)
S(1)-Co(1)-S(2)	128.000(14)	119.34(5)	
Si(1)-S(1)-Co(1)	108.485(17)	112.69(7)	107.85(9)
Si(2)-S(2)-Co(1)	104.548(17)	100.24(6)	

Symmetry code: (#) -x+1,y,-z+3/2

Table S3. Parameters of the hydrogen bonds in the complexes **1**-**2**.

Compound	Bond	D-H (Å)	H···A (Å)	D···A (Å)	<DHA (°)
1	N(1)-H(1)··O(2)	1.00	2.17	3.0407(14)	145.0
	N(2)-H(2)··O(6)	1.00	2.48	3.2196(15)	130.3
2	N(1)-H(1A)···O(4)	0.91	2.44	3.292(5)	155.7
	N(1)-H(1B)···O(1)	0.91	2.19	3.007(6)	148.7
	N(2)-H(2)···O(6)	1.00	2.07	2.941(5)	144.8
	N(1)-H(1C)···N(3)			3.108(7)	

Table S4. Geometric indexes τ_4 and τ'_4 indicating the tetrahedral geometry of the coordination Co(II) centers in complexes **1**-**3**.

geometric index	compound		
	1	**2**	**3**
τ_4	0.82	0.92	0.89
τ'_4	0.78	0.89	0.84

Table S5. The comparison of the closest Co···Co distances in the crystal packing of complexes **1**-**3**.

compound	**1**	**2**	**3**
Co···Co distance [Å]	7.8741(8)	10.491(1)	9.401

Table S6. The torsion angles in complexes **1**-**3**.

1	
S(1)-Co(1)-S(2)-Si(2)	60.07(2) °
S(2)-Co(1)-S(1)-Si(1)	167.121(17) °
2	
S(1)-Co(1)-S(2)-Si(2)	-169.83(6) °
S(2)-Co(1)-S(1)-Si(1)	103.64(8) °
3	
S(1)#1-Co(1)-S(1)-Si(1)	-171.02(11) °

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2

2. SUPPORTING FIGURES

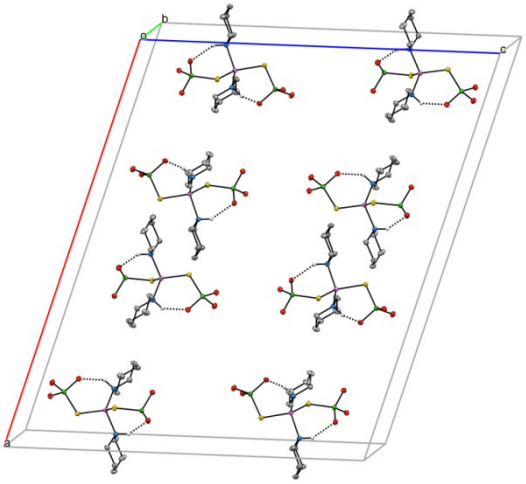

Fig. S1. The crystal packing of **1** along axis. *t*BuO groups and hydrogen atoms of C-H bonds omitted for clarity.

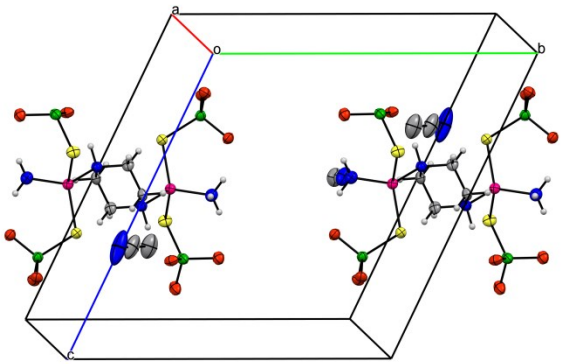

Fig. S2. The crystal packing of **2** along *b* axis, *t*BuO groups omitted for clarity.

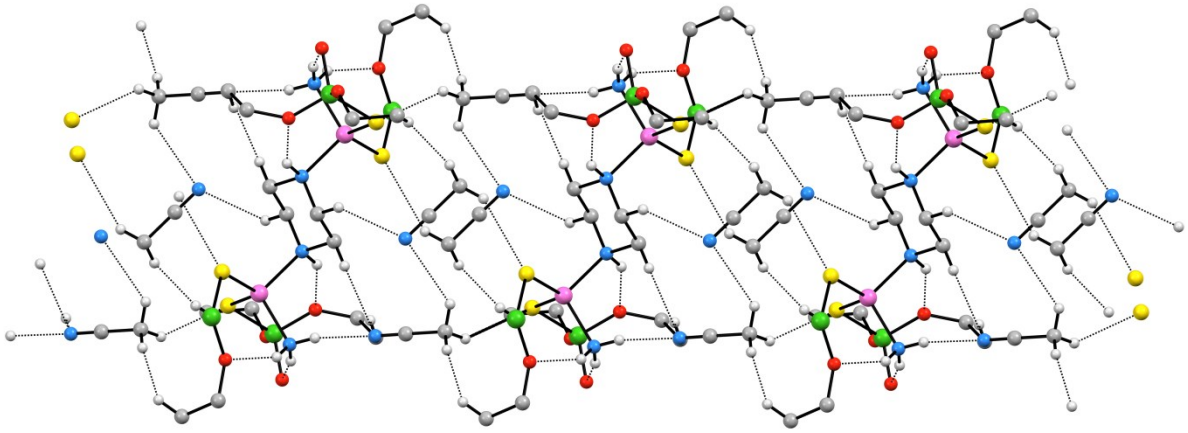

Fig. S3. The net of intra- and intermolecular interactions shown as a dashed lines present in complex **2**.

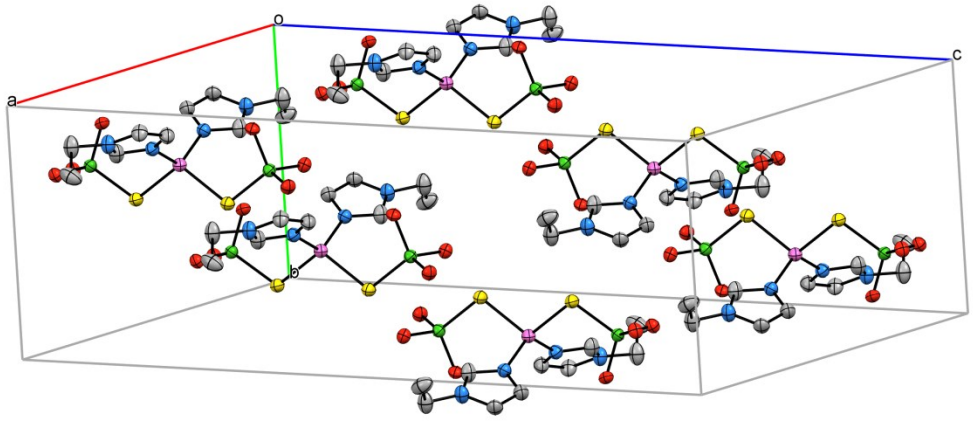

Fig. S4. The crystal packing of **3** along *c* axis, *t*BuO groups omitted for clarity.

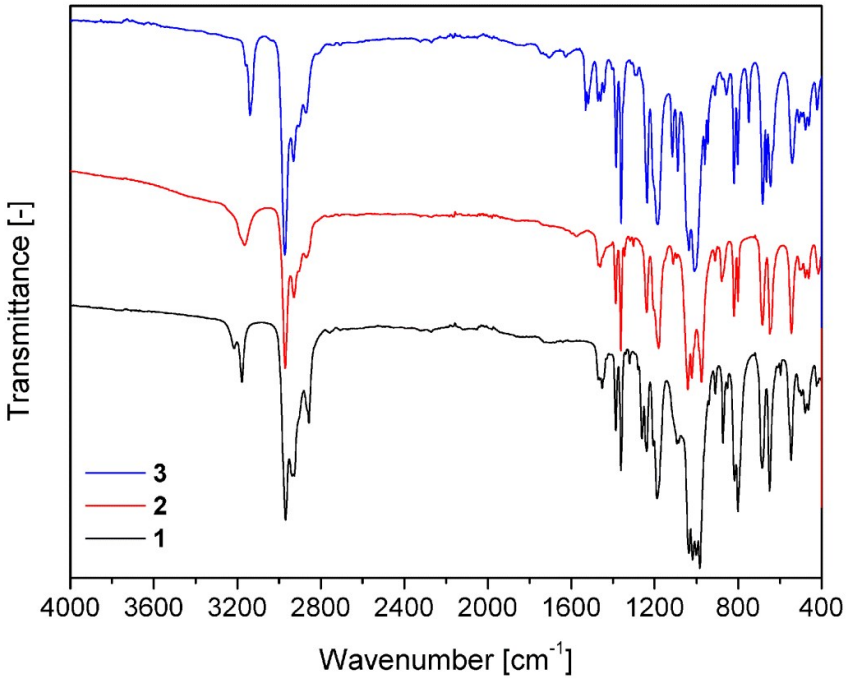

Fig. S5. FTIR spectrum of complex **1-3** in the range of 4000-400 cm^{-1}.

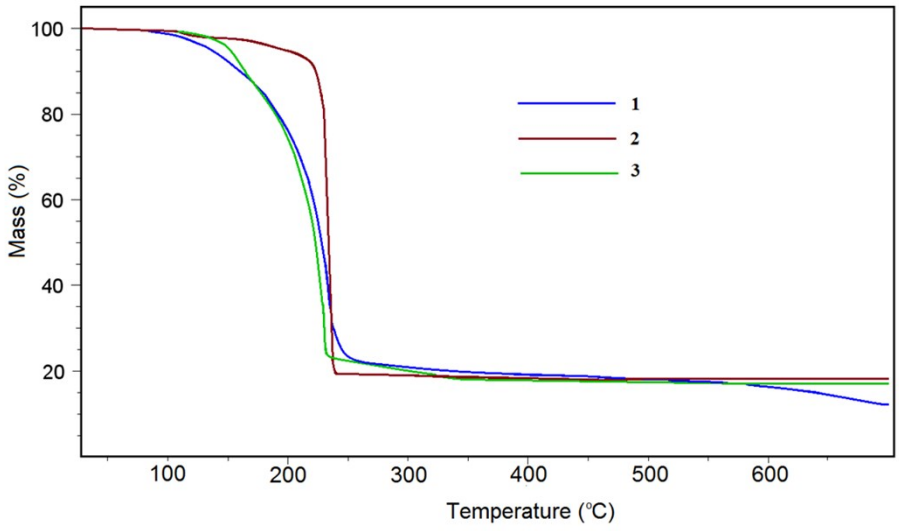

Fig. S6. TG curves of **1**-**3** complexes in nitrogen.

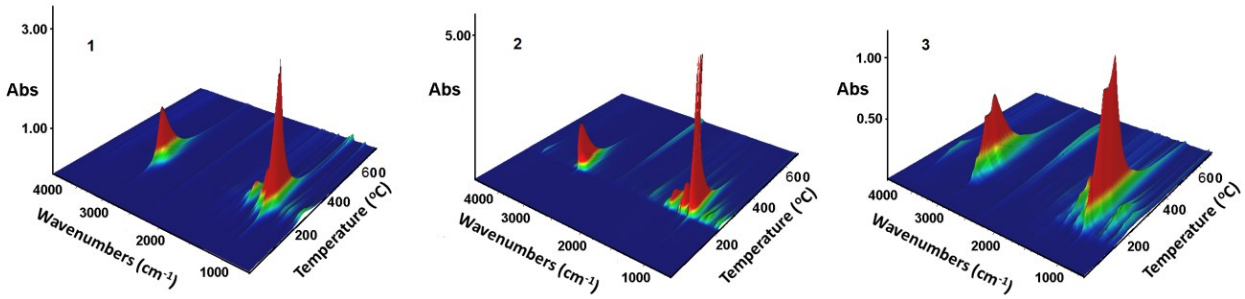

Fig. S7. Stacked plot of FTIR spectra of the evolved gases for **1**-**3** complexes.

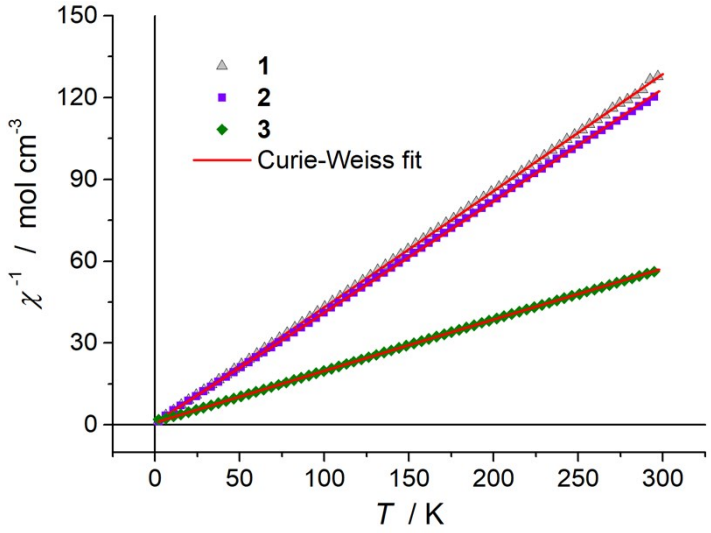

Fig. S8. Temperature dependences of reciprocal molar susceptibility, χ^{-1}, for **1** - **3**, measured at 1 kOe (*symbols*) and Curie-Weiss fits to the data (*solid lines*).

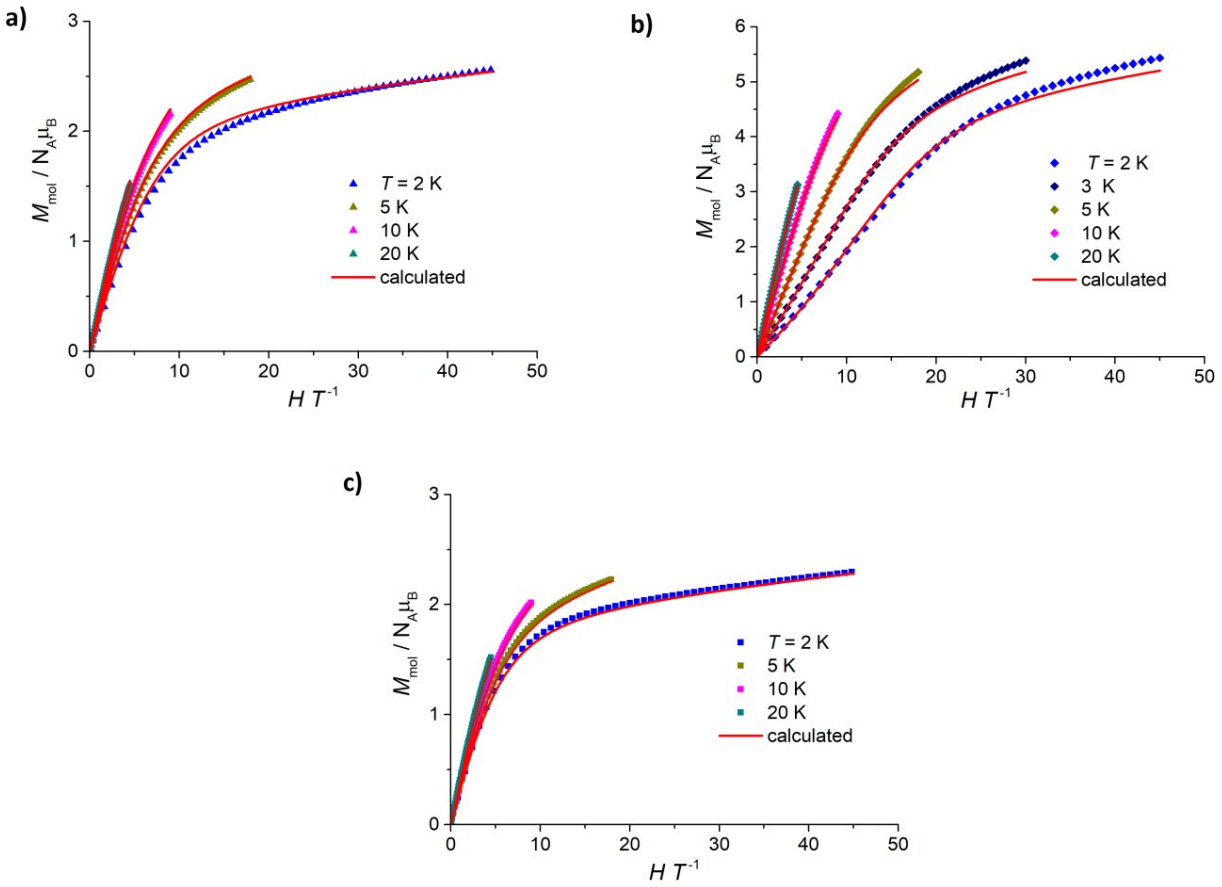

Fig. S9. Experimental (*symbols*) and calculated (*solid lines*) low-temperature magnetization curves in reduced coordinates $M_{mol}/\mu_B N_A$ *vs* H/T for samples **1** (a), **2** (b) and **3** (c). The models used for simulations and best-fitting parameter values are described in the text.

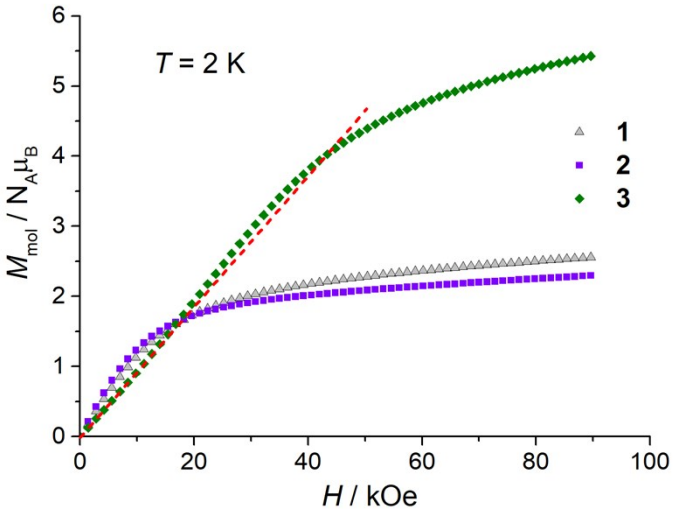

Fig. S10. Magnetization curves for samples **1**, **2** and **3** measured at 2 K.

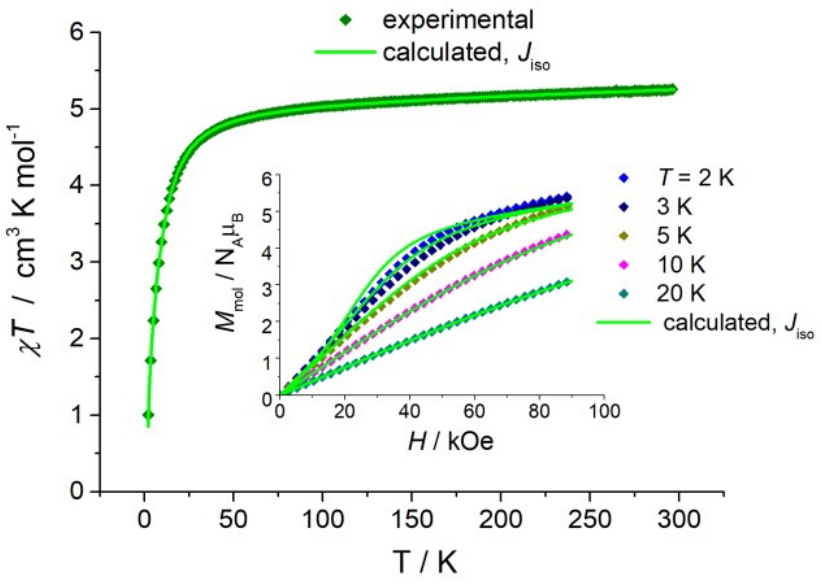

Fig. S11. Plot of χT versus *T*, measured at 1 kOe, and magnetization curves (inset) measured at 2, 3, 5, 10, and 20 K for **2** (*symbols*). Solid lines represent the calculation results with model described by equation (2), in which isotropic spin-spin interaction *J* have been considered; the best-fitting parameter values are given in the text.