Novel tetrahedral cobalt(II) silanethiolates: a variety of structures and magnetic properties

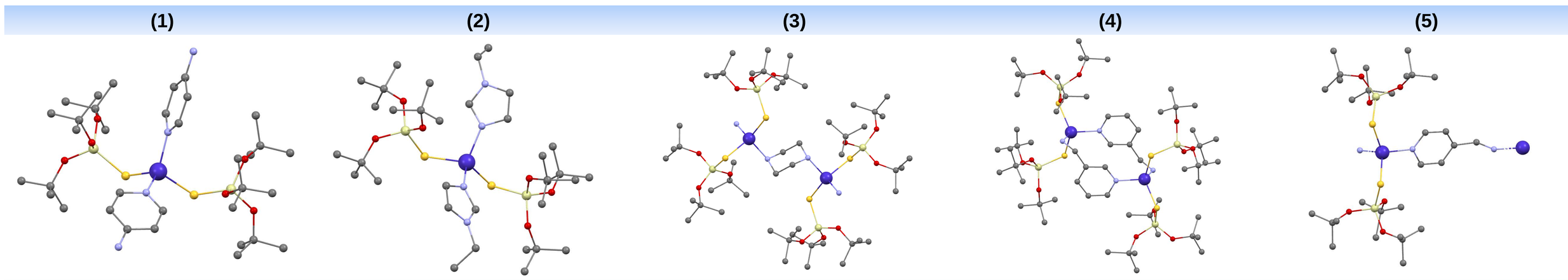
N. Nedelko*[a], P. Aleshkevych[a], D. Kowalkowska-Zedler[b], A. Pladzyk[b] and A. Ślawska-Waniewska[a]

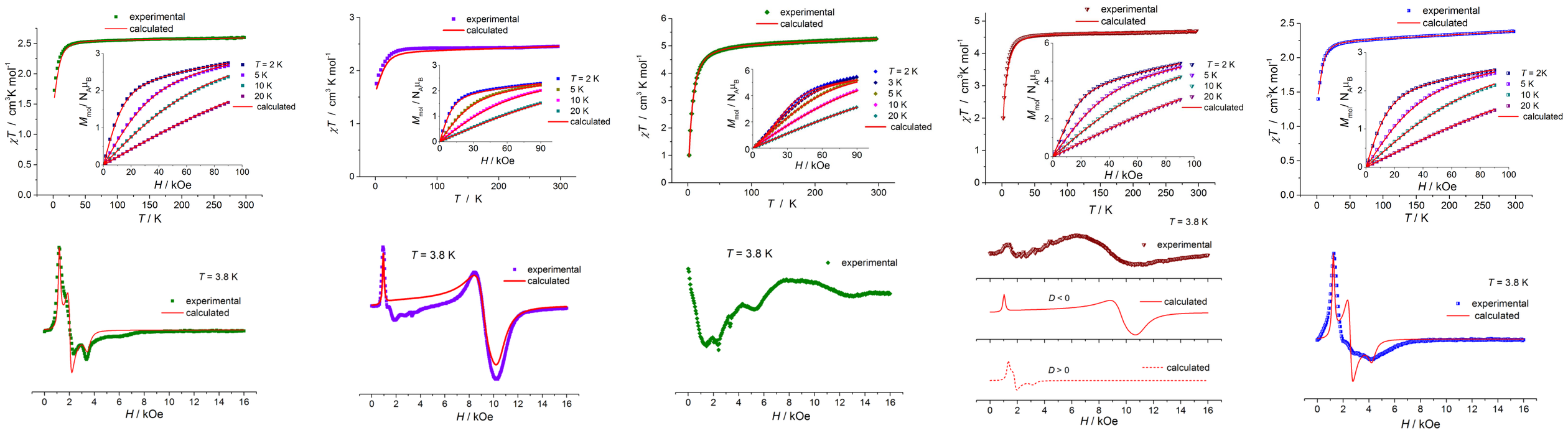
[a] Institute of Physics, Polish Academy of Sciences, Warsaw (* natal@ifpan.edu.pl)

[b] Department of Inorganic Chemistry, Faculty of Chemistry, University of Technology, Gdańsk

A group of new heteroleptic Co(II) silanethiolates has been investigated using static (*dc*) and dynamic (*ac*) magnetic measurements as well as X-band EPR spectroscopy

The complexes contain Co(II) ions in a tetrahedral N_2S_2 environment and present variable structures: **1** and **2** are mononuclear, **3** and **4** are dinuclear and **5** is 1D coordination polymer





Top: Plots of χT *versus* T measured at 1 kOe for polycrystalline powdered samples and isothermal magnetization curves measured at 2, 5, 10 and 20 K (*insets*). **Bottom:** X-band EPR powder spectra recorded at 3.8 K. In all panels, symbols represent the experimental data whereas solid red lines – best-fit simulations according to eqn **(a)** for **1**, **2**, and **5** or eqn **(b)** for **3** and **4**, with parameters given in the following **Table**.

$$\mathcal{H} = D\left[\hat{S}_z^2 - S(S+1)/3\right] + E\left[\hat{S}_x^2 - \hat{S}_y^2\right] + \mu_B \mathrm{Hg}\hat{S} \qquad \textbf{(a)}$$

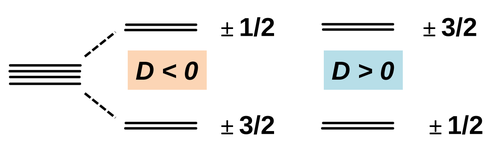
$$\mathcal{H} = -2J\hat{S}_1\hat{S}_2 + D\sum_{i=1,2}\left[\hat{S}_{zi}^2 - S(S+1)/3\right] + E\sum_{i=1,2}\left[\hat{S}_{xi}^2 - \hat{S}_{yi}^2\right] + \mu_B \mathrm{Hg}\sum_{i=1,2}\hat{S}_i \qquad \textbf{(b)}$$

D and *E* denote the second-order axial and rhombic Zero-Field Splitting (ZFS) parameters, respectively

	D, cm $^{-1}$	|D/E|	g_x	g_y	g_z
1	9.00	0.22	2.53	2.20	2.25
2	-17.00	0.11	2.38	1.88	2.39
3	|9.43|	-	g_{iso}= 2.33		
4	-11.10	0.10	g_{iso}= 2.22		
5	8.14	0.30	2.42	2.04	2.05

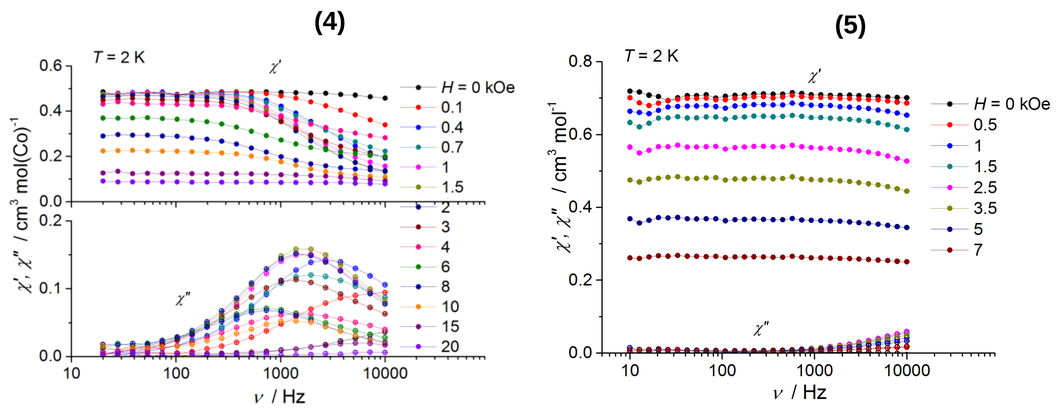
Co(II): $3d^7$, S = 3/2, L = 3

the ground states: m_S= ± 1/2; ± 3/2



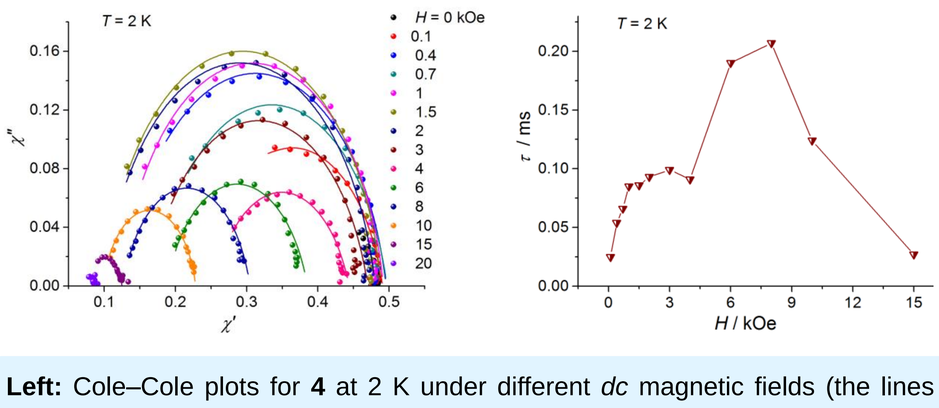
in distorted tetrahedral geometry

$J_{12} \approx$ - 0.62 cm^{-1} and $J_{12} \approx$ - 0.13 cm^{-1} for **3** and **4**, respectively



Frequency-dependent in-phase χ' and out-of-phase χ'' *ac* susceptibility data, for **4** (left) and **5** (right), measured under different *dc* magnetic field, at 2 K (lines are guide to the eye).

In a high temperature range, the obtained data of all complexes show a behavior typical of paramagnetic high–spin Co(II) ions. At low temperatures, weak Co–Co intra-molecular AFM interactions were detected in complexes **3** and **4**. However, it was also shown that the low-temperature magnetic behavior of all complexes is defined by the ZFS effect. The modeling of the magnetic and EPR data was done to estimate ZFS parameters. The obtained results show that studied complexes, regardless of similarity in structure of the CoN_2S_2 cores, have different types of local magnetic anisotropy: *easy-plane* and *easy-axis* for **1**, **5** and **2**, **4**, respectively. A comparative magneto-structural analysis of these complexes points to the high sensitivity of the single-ion magnetic anisotropy of tetrahedrally coordinated cobalt ions to subtle changes in the first and second coordination spheres of Co(II)



Left: Cole–Cole plots for **4** at 2 K under different *dc* magnetic fields (the lines show the best fits using the generalized Debye model). **Right:** Field dependences of the spin–lattice relaxation time τ, estimated for **4** at 2 K.

All complexes were also probed for Single Ion Magnets (SIMs) behavior. In the absence of a static magnetic field, all of them were found to display fast magnetic relaxations. Upon applying an external static magnetic field, a pronounced slow relaxation behavior, characteristic of field-induced SIMs, has been found for **1**, **2** and **4**

Published in : Dalton Transactions 49, 697-710 (2020) ; RSC Advances 10, 29100 (2020)