

## Diamagnetic cobalt(III)tris(o-ethylxanthate) and nickel(II)bis(o-ethylxanthate)

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### Abstract

Diamagnetic [Co(*xanth*)<sub>3</sub>] and [Ni(*xanth*)<sub>2</sub>] complexes have been prepared by reaction of Co(II) and Ni(II) salts with potassium *O*-ethyl xanthate (*Kxanth*). The isolated Co(III) and Ni(II) complexes have been characterized by single-crystal X-ray crystallography, UV-VIS and IR spectroscopy, computational methods, and magnetic measurements.

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## Introduction

Transition metal complexes containing chelating ligands are the subjects of extensive research for a long time due to the broad range of their structural, spectral and magnetic properties (Gerloch and Constable 1994). In the past few decades, such coordination compounds have attracted increased attention of chemists because of their potential applications in various fields as chemical sensors, nonlinear optical materials and/or molecular magnetic materials (Noro *et al.* 2009).

Over the past ten years, an extraordinary interest on single-molecule magnets (SMMs) has been registered. Single-molecule magnets, attractive for high-density information storage and quantum computing, are metal complexes, that beside other interesting quantum phenomena, exhibit slow relaxation of the magnetization. The earlier type of SMMs was based on high-spin polynuclear complexes, such as a dodecanuclear plaquette-type complex known as Mn<sub>12</sub>ac. In course of time a

plethora 3d-metal complexes were identified as SMMs, including simple mononuclear systems containing Mn(III) (Grigoropoulos *et al.* 2013), Fe(III) (Mossin *et al.* 2012), Fe(II) (Feng *et al.* 2013), Fe(I) (Samuel *et al.* 2014), Co(II) (Rajnák *et al.* 2017), Ni(II) (Lomjansky *et al.* 2017), Ni(I) (Lin *et al.* 2016) and Cu(II) (Boča *et al.* 2017) central atoms (Frost *et al.* 2016). Among these systems, the S-donor ligands combined with the cobalt(II) centres attract a considerable attention because of the pronounced magnetic anisotropy that supports the SMM behaviour (Zdrozny and Long 2011). However, Co(II) can be readily oxidized to Co(III) in course of the complexation reaction on air giving rise the diamagnetic complex. Tetracoordinate Ni(II) complexes in their nearly tetrahedral geometry are also promising SMMs. Some ligands prefer the square planar arrangement around the Ni(II) central atom and these complexes are diamagnetic as well. Some relationships between the structure and magnetic properties are compared in Table 1. Herein we are

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**Table 1.** Comparison of structure-magnetism relationships for related compounds.

Complex	Chromophore	Magnetic property	Reference
(Ph <sub>4</sub> P) <sub>2</sub> [Co(SPh) <sub>4</sub> ]	Tetrahedral	SMM	Zadrozny and Long 2011
[Co(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	Tetrahedral	SMM	Yang <i>et al.</i> 2013
[Co(PPh <sub>3</sub> ) <sub>2</sub> Br <sub>2</sub> ]	Tetrahedral	SMM	Boča <i>et al.</i> 2014
[Co(PPh <sub>3</sub> ) <sub>2</sub> I <sub>2</sub> ]	Tetrahedral	SMM	Saber and Dunbar 2014
[Co(PPh <sub>3</sub> ) <sub>2</sub> (SCN) <sub>2</sub> ]	Tetrahedral	SMM	Rajnák <i>et al.</i> 2016
[Ni(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	Tetrahedral	Paramagnet, no SMM	Lomjanský <i>et al.</i> 2016
[Ni(PPh <sub>3</sub> ) <sub>2</sub> (NCS) <sub>2</sub> ]	Planar	Diamagnet, no SMM	Rajnák, unpublished

reporting about synthesis, characterization and structural properties of the [Co(*xanth*)<sub>3</sub>] and [Ni(*xanth*)<sub>2</sub>] complexes with chelating S-donor ligand which were found to be diamagnetic.

## Experimental

### Chemicals and handling

All inorganic and organic reactants of reagent grade quality were purchased and used as received (Sigma-Aldrich). The solvents ethanol and acetonitrile were used without further purification.

### Synthesis of [Co(*xanth*)<sub>3</sub>] (1)

The compound **1** has been prepared as follows. 0.16 g (1 mmol) of potassium *O*-ethyl xanthate, was dissolved in ethanol (10 cm<sup>3</sup>) under an intense stirring. 0.064 g of cobalt(II) chloride was also dissolved in 10 cm<sup>3</sup> of ethanol under an intense stirring (the molar ratio of *xanth*: cobalt(II) chloride = 2:1). The two solutions were mixed and the final solution was refluxed for 4 hours. The filtrate was left for the duration of 5 days for a spontaneous evaporation. Deep dark green crystals were obtained by slow evaporation of the solution at room temperature. Yield: 0.085 g Anal. Calc. for 1, C<sub>9</sub>H<sub>15</sub>CoO<sub>3</sub>S<sub>6</sub> (*M* = 422.57 g mol<sup>-1</sup>): C, 25.58; H, 3.58; S, 45.53. Found: C, 25.88; H, 3.56; S, 46.02. Selected IR bands (KBr)  $\nu/\text{cm}^{-1}$ : 2976(w), 2484(w), 1898(w), 1861(w), 1721(w), 1464(w), 1444(m), 1433(m), 1387(m), 1365(s), 1273(w), 1233(s), 1143(w), 1116(s), 1055(w), 1030(s), 1000(s), 861(m), 810(w), 657(w), 548(w), 438(s). UV/Vis (Nujol)  $\nu_{\text{max}}/10^3 \text{ cm}^{-1}$  (relat. absorb.): 15.8 (0.435), 20.7 (0.526).

### Synthesis of [Ni(*xanth*)<sub>2</sub>] (2)

The compound **2** was prepared as follows. A 100 cm<sup>3</sup> round bottom flask was charged with potassium ethyl xanthogenate (0.150 g, 0.94 mmol) and acetonitrile (20 cm<sup>3</sup>) and slight heated. NiCl<sub>2</sub>·6H<sub>2</sub>O (0.111 g, 0.47 mmol) was added once. Yellowish solution changed colour immediately to green. Reaction was heated with an oil bath for four hours at 80°C. In process of cooling a mixture changed colour to brown. After 3 days dark red crystalline compound was filtered off and dried in vacuum. Yield: 0.026 g. Anal. Calc. for 1, C<sub>6</sub>H<sub>10</sub>NiO<sub>2</sub>S<sub>4</sub> (*M* = 301.10 g mol<sup>-1</sup>): C, 23.93; H, 3.35; S, 42.60. Found: C, 24.14; H, 3.05; S, 41.13. Selected IR bands (KBr)  $\nu/\text{cm}^{-1}$ : 2982(w), 2935(w), 2891(w), 2503(w), 1464(m), 1429(w), 1388(w), 1366(s), 1325(w), 1244(s), 1144(w), 1113(s), 1058(w), 1020(s), 996(s), 855(m), 808(w), 662(w), 554(w), 435(s) (s – strong, m – medium, w-weak); S-C=S (554 cm<sup>-1</sup>), C=S (1058 – 1144 cm<sup>-1</sup>), C-O-C (855 cm<sup>-1</sup>),  $\nu\text{CH}_3$  (2935 cm<sup>-1</sup>),  $\nu\text{CH}_2$  (2891 cm<sup>-1</sup>) a  $\delta\text{C-H}$  (1325 – 1464 cm<sup>-1</sup>). UV/Vis (Nujol)  $\nu_{\text{max}}/10^3 \text{ cm}^{-1}$  (relat. absorb.): ~15.0 (0.191), 20.7 (0.459), 23.8 (0.513).

### Physical measurements

Elemental analyses were carried out by Flash 2000 CHNS apparatus (Thermo Scientific). The IR spectra were measured on ATR holder with highly effective diamond crystal in the region of 4000 – 400 cm<sup>-1</sup> by Nicolet 5700 spectrometer (Thermo Electron) with DTGS/KBr detector. The solid sample for FT-IR measurements was not dried prior to its using and was used as freshly synthesized. Absorption UV-Vis spectra for solid sample (Nujol mull) were measured by Specord.

**Table 2.** Crystal data and structure refinement for **1**, **2**.

Empirical formula	C <sub>9</sub> H <sub>15</sub> CoO <sub>3</sub> S <sub>6</sub>	C <sub>6</sub> H <sub>10</sub> NiO <sub>2</sub> S <sub>4</sub>
Formula weight (g.mol <sup>-1</sup> )	422.50	301.09
Crystal system	trigonal	orthorhombic
Space group	<i>R</i> -3	<i>Pbca</i>
<i>T</i> (K)	100(1)	100(1)
<i>a</i> (Å)	14.8164(14)	7.4174(8)
<i>b</i> (Å)	14.8164(14)	7.1003(6)
<i>c</i> (Å)	12.8790(12)	20.760(2)
$\alpha$ (°)	90	90
$\beta$ (°)	90	90
$\gamma$ (°)	120	90
<i>V</i> (Å <sup>3</sup> )	2 448.5(5)	1 093.36(19)
$\rho_{\text{calc}}$ (g.cm <sup>-3</sup> )	1.719	1.829
<i>Z</i>	6	4
Radiation type	Cu K $\alpha$	Cu K $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.54186	1.54186
<i>F</i> (000)	1 296	616
Abs. coefficient	15.426	9.439
<i>R</i> <sub>1</sub> [ <i>F</i> 2 > 2 $\sigma$ ( <i>F</i> 2)], <i>wR</i> <sub>2</sub> ( <i>F</i> 2)	0.0328, 0.0755	0.0476, 0.1220
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.45, -0.59	1.45, -0.45
CCDC no.	1569076	1569077

250 Plus (Analytica Jena) with the DAD detector in the range of 9 000 – 50 000 cm<sup>-1</sup>. Magnetic data was taken with the SQUID apparatus (Quantum Design, MPMS-XL7) in the RSO mode of the detection. The detected magnetic moment of the specimen has been converted to the molar magnetic susceptibility  $\chi_{\text{mol}}$  and the dimensionless product function  $\chi T/C_0$  with the reduced Curie constant  $C_0 = N_A \mu_0 \mu_B^2 / k_B$  containing the fundamental physical constants in their usual meaning.

#### *X-ray crystal structure determination*

Data collection and cell refinement of **1**, **2** were made by Stoe StadiVari diffractometer using PILATUS3R 300K HPAD detector and micro-focused source Xenocs FOX3D with CuK $\alpha$  at 100K. Corrections to Lorentz, polarization and multi-scan absorption effects were applied. The structure was solved by charge-flipping or direct methods and refined anisotropically by common least-squares methods. The programs SUPERFLIP (Palatinus and Chapuis 2007), SHELXT (Sheldrick 2015), SHELXL (ver. 2016/6) (Sheldrick 2015) and OLEX2 (Dolomanov *et al.* 2009) have been used for structure determination, refinement and drawing. The hydrogen atoms were refined with fixed distances from the parent carbon atoms. Crystal data on **1**, **2** are presented in Table 2.

## Results and Discussion

### *Structural data*

The compound **1**, [Co(*xanth*)<sub>3</sub>], possesses a molecular structure. The central Co(III) atom is hexacoordinate by three bidentate *xanth* ligands (Fig. 1). The Co-S distances are almost identical (2.268 – 2.282 Å, see Table 3). As expected, the S-Co-S angles are acute (41 – 51 deg). The compound **1**, [Co(*xanth*)<sub>3</sub>], crystallizes in trigonal system in space group *R*-3. The cobalt atom lies on 3-fold axis and is coordinated in distorted octahedron. The coordination octahedron around cobalt atom of **1** is formed by six sulfur atoms [Co1-S1 = 2.2693(7) Å and Co1-S2 = 2.2743(8) Å (Table 3)] of three bidentate carbamate group of *xanth*.

The compound **2**, [Ni(*xanth*)<sub>2</sub>] crystallize in orthorhombic system in space group *Pbca* (Table 2) and it possesses a molecular structure with the planar chromophore {Ni<sup>II</sup>S<sub>4</sub>} – see Fig. 2. The nickel atom lies in the centre of symmetry and is bonded by four sulfur atoms [Ni1-S distance in region 2.21– 2.22 Å (Table 4)] of two bidentate carbamate groups of *xanth* square-planar coordination.

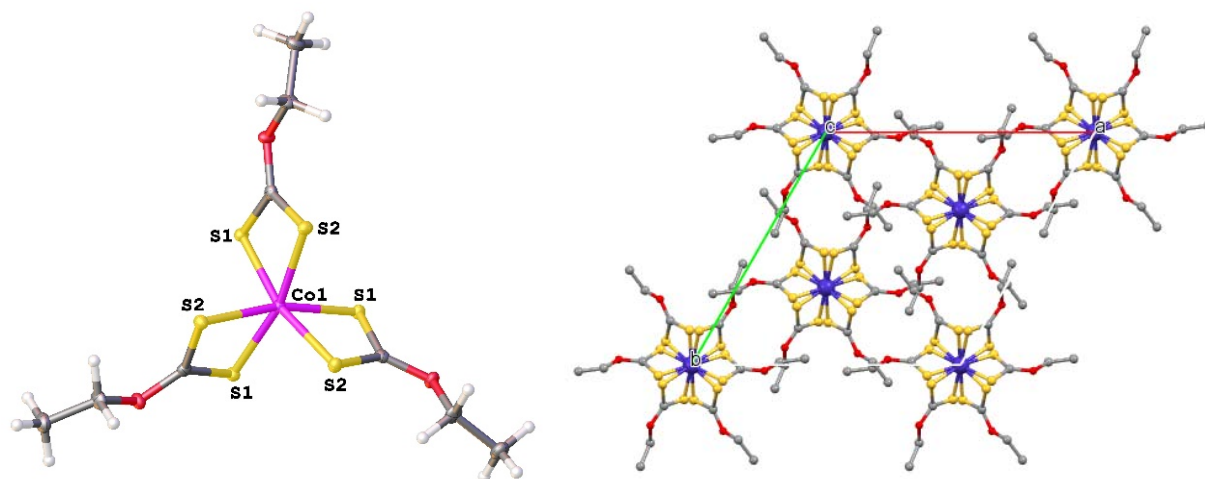


Fig. 1. Molecular and crystal structure of complex  $[\text{Co}(\text{xanth})_3]$ , **1**.

Table 3. Selected bond lengths (Å) and angles (°) in complex **1**.

Co1–S1	2.2693(7)	Co1–S2	2.2743(8)
Co1–S1 <sup>i</sup>	2.2693(7)	Co1–S2 <sup>i</sup>	2.2743(8)
Co1–S1 <sup>ii</sup>	2.2693(7)	Co1–S2 <sup>ii</sup>	2.2744(8)
S1–Co1–S1 <sup>i</sup>	94.18(3)	S1–Co1–S1 <sup>ii</sup>	94.19(3)
S1 <sup>i</sup> –Co1–S1 <sup>ii</sup>	94.19(3)	S1 <sup>ii</sup> –Co1–S2 <sup>i</sup>	166.63(2)
S1–Co1–S2	76.73(2)	S1 <sup>i</sup> –Co1–S2	166.63(2)
S1–Co1–S2 <sup>ii</sup>	166.63(2)	S1 <sup>i</sup> –Co1–S2 <sup>ii</sup>	96.22(2)
S1 <sup>i</sup> –Co1–S2 <sup>i</sup>	76.73(2)	S1–Co1–S2 <sup>i</sup>	96.22(2)
S1 <sup>ii</sup> –Co1–S2 <sup>ii</sup>	76.73(2)	S1 <sup>ii</sup> –Co1–S2	96.22(2)
S2 <sup>i</sup> –Co1–S2	94.31(3)	S2 <sup>i</sup> –Co1–S2 <sup>ii</sup>	94.31(3)
S2–Co1–S2 <sup>ii</sup>	94.31(3)		

Symmetry codes: (i)  $1-y, x-y, z$ ; (ii)  $1+y-x, 1-x, z$

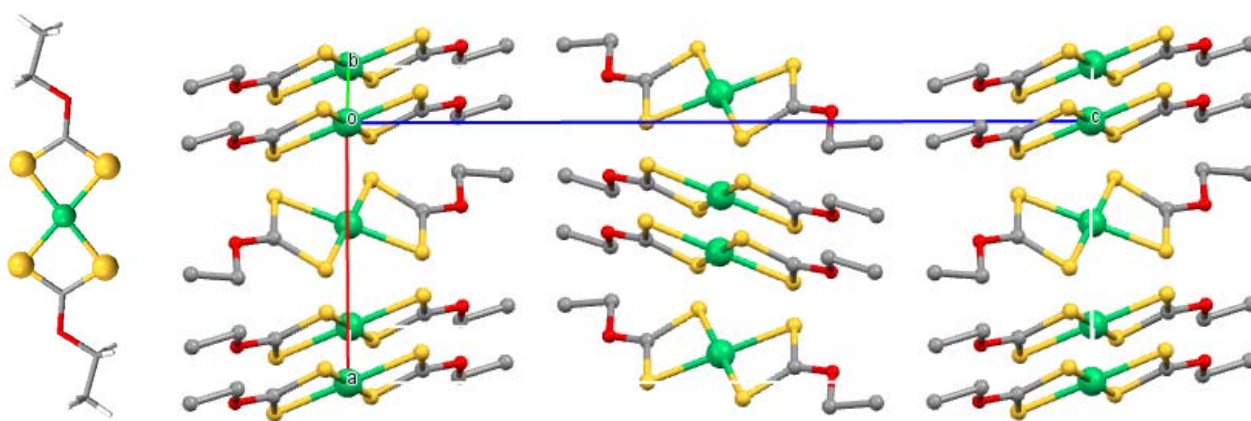


Fig. 2. Molecular and crystal structure of the complex  $[\text{Ni}(\text{xanth})_2]$ , **2**.

### Electronic spectra

The solid state electronic spectra of **1** and **2** measured in Nujol mull are presented in Fig. 3. These complexes exhibit a similar spectral profile

with a number of electronic transitions that have varying peak intensity. The first visible transitions are slightly intense and located in the range of  $15\,000 - 25\,000\text{ cm}^{-1}$ . This part of the spectrum is almost identical for both complexes. In this range

we can identify two transitions at  $\sim 15\,000$  and  $20\,000\text{ cm}^{-1}$ . Moreover, in the spectrum of the Ni(II) complex another peak is visible at  $\sim 24\,000\text{ cm}^{-1}$ . For the Co(III) complex this transition is missing, however, there is a broad asymmetric band in this location with a maximum at  $28\,000\text{ cm}^{-1}$ . More intense and clearly identifiable peaks are located in the range of  $30\,000 - 50\,000\text{ cm}^{-1}$ .

**Table 4.** Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) in complex **2**.

Ni1-S1	2.2182(8)
Ni1-S1 <sup>iii</sup>	2.2183(8)
Ni1-S2	2.2201(7)
Ni1-S2 <sup>iii</sup>	2.2201(7)
S1-Ni1-S1 <sup>iii</sup>	180.0
S1-Ni1-S2	79.43(3)
S1 <sup>iii</sup> -Ni1-S2 <sup>iii</sup>	79.43(3)
S1 <sup>iii</sup> -Ni1-S2	100.57(3)
S1-Ni1-S2 <sup>iii</sup>	100.57(3)
S2-Ni1-S2 <sup>iii</sup>	180.0

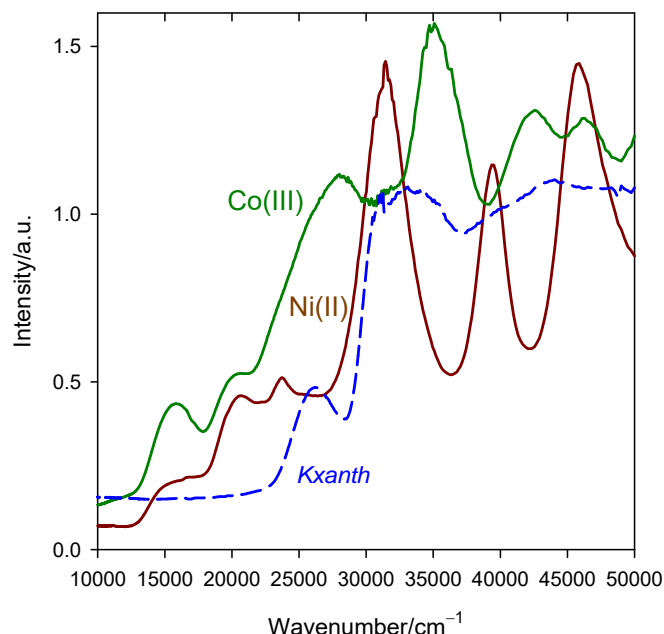
Symmetry codes: (iii) 1-x, -y, 1-z; (iv) -x, 1-y, -z

The hexacoordinate Co(III) complexes in the strong crystal field possess the electronic ground term  $^1A_{1g}$  that is well separated from its excited counterparts. A modelling using the generalized crystal-field theory (GCFT) with the crystal field poles  $F_4 = 20\,000\text{ cm}^{-1}$  ( $10Dq = 33\,333\text{ cm}^{-1}$ ) lifts the first spin-allowed d-d transition to  $E_1 = 26\,000\text{ cm}^{-1}$  ( $^1A_{1g} \rightarrow ^1T_{1g}$ ) and the second one to  $E_2 = 28\,000\text{ cm}^{-1}$  ( $^1A_{1g} \rightarrow ^1T_{2g}$ ). The square-planar Ni(II) complexes in the strong crystal field also possess the electronic ground term  $^1A_{1g}$ . A modelling by the GCFT with the crystal field poles  $F_2 = 20\,000$  and  $F_4 = 10\,000\text{ cm}^{-1}$  gave the lowest spin-allowed excitation energies at  $E_1 = 14\,900\text{ cm}^{-1}$  ( $^1A_{1g} \rightarrow ^1A_{2g}$ ) and  $E_2 = 21\,300\text{ cm}^{-1}$  ( $^1A_{1g} \rightarrow ^1B_{1g}$ ). *Ab initio*

**Table 5.** Assignment of transitions in **1** and **2**.

<b>1</b>		<b>2</b>	
experimental	<i>ab initio</i>	experimental	<i>ab initio</i>
11000 w	13500 $^3T_{1g}$		2800 – 4300
16000 m	18100 $^5T_{2g}$	13500 sh	13500 $^3E_g$
20500 m	19400 $^3T_{2g}$	16000 m	16700, 17800,
28000 s	21500 $^1T_{1g}$	20600 m	18200
31500 s	32800 $^1T_{2g}$	23700 m	23400 $^3B_{2g}$ , 23400
35000 s	34400 $^3T_{2g}$	31500 s	
36500 s	36500 $^3T_{1g}$	39500 s	36000

w – weak, m – medium, s – strong, sh – shoulder



**Fig. 3.** Solid state electronic spectra for complexes **1** and **2**. Spectrum of the *Kxanth* is added for comparison.

calculations based on multireference CASSCF method improved by NEVPT2 approach have been performed to verify the crystal-field theory results. To this end, the active space extended by the second d-shell ( $n$  electrons, where  $n = 6$  for Co(III) and 8 for Ni(II), were correlated in 10 orbitals) and def2-TZVP basis set were used within these calculations. Averaging of 10 triplet and 15 singlet states of Ni(II) and 5 quintet, 45 triplet and 50 singlet states of Co(III) was utilized. The results obtained for the experimental geometry of complexes are collected in Table 5. It can be seen, the agreement between the GCFT and *ab initio* results is good (Table 6). Thus, estimation of the crystal field poles in the previous analysis and the conclusions that follow may be considered correct. Comparison of the calculated results with the experimental spectra also confirms this claim.

**Table 6.** Calculated transition energies below 50 000 cm<sup>-1</sup> for **1** and **2**<sup>a</sup>.

<b>1, [Co(<i>xanth</i>)<sub>3</sub>]</b>				<b>2, [Ni(<i>xanth</i>)<sub>2</sub>]</b>			
Term	GCFT Energy	CASSCF-NEVPT2 Mult.	CASSCF-NEVPT2 Energy	Term	GCFT Energy	CASSCF-NEVPT2 Mult.	CASSCF-NEVPT2 Energy
<sup>1</sup> A <sub>1g</sub>	0	1	0	<sup>1</sup> A <sub>1g</sub>	0	1	0
<sup>5</sup> T <sub>2g</sub>	15095 15095	3	13433	<sup>3</sup> B <sub>1g</sub>	4179	3	2770
	15095 16003	3	13471	<sup>3</sup> A <sub>2g</sub>	4554	3	2967
	16003 16003	3	13487	<sup>3</sup> E <sub>g</sub>	7588	3	4288
<sup>3</sup> T <sub>1g</sub>	16045 16045	5	18097		7588	3	13502
	16045 26046	5	18126	<sup>1</sup> A <sub>2g</sub>	14900	1	16677
	26046 26046	5	18158	<sup>3</sup> B <sub>2g</sub>	20846	1	17813
<sup>3</sup> T <sub>2g</sub>	28160 28160	3	19305	<sup>1</sup> B <sub>1g</sub>	21277	1	18257
	28160 39708	3	19454	<sup>1</sup> E <sub>g</sub>	23443	3	23399
	39708 39708	3	19461		23443	1	23438
	39738 39738	1	21442	<sup>3</sup> E <sub>g</sub>	23970	3	24332
<sup>1</sup> T <sub>1g</sub>	39738 43430	1	21459		23970	3	25556
	43430 45803	1	21479	<sup>1</sup> A <sub>1g</sub>	31317	3	26762
	45803 45803	1	32393	<sup>1</sup> B <sub>2g</sub>	37520	3	36081
<sup>1</sup> T <sub>2g</sub>	46315 46315	1	32891	<sup>3</sup> A <sub>2g</sub>	38958	1	37096
	46315 48429	1	32907	<sup>1</sup> E <sub>g</sub>	41225	3	37965
	48429	3	34281		41225	1	40728
<sup>3</sup> T <sub>2g</sub>	49973 49973	3	34386	<sup>3</sup> E <sub>g</sub>	45180	1	40795
	49973	3	34406		45180	1	41733
		3	36540				
<sup>3</sup> T <sub>1g</sub>		3	36548				
		3	36602				
		5	39661				
<sup>3</sup> E <sub>g</sub>		5	39671				
		3	41659				
<sup>3</sup> T <sub>1g</sub>		3	41664				
		3	41710				
		3	41740				
<sup>3</sup> T <sub>2g</sub>		3	41742				
		3	41852				
		3	42923				
<sup>5</sup> E <sub>g</sub>		3	42941				
		1	44395				
<sup>1</sup> T <sub>2g</sub>		1	44445				
		1	44597				
		1	45531				
		1	45586				
		1	47628				
		1	47628				

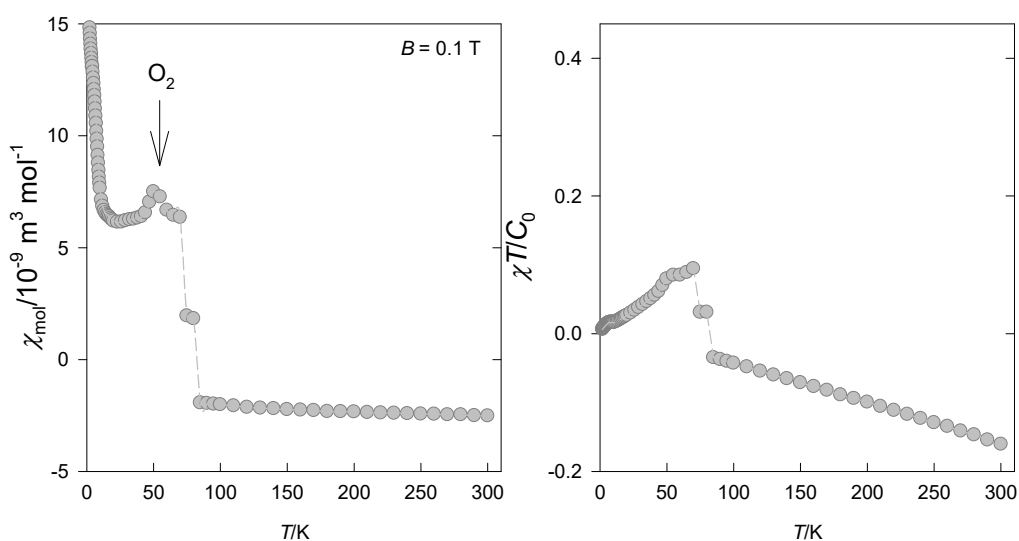
<sup>a</sup> GCFT calculations in an idealized octahedral (square planar) geometry; *ab initio* CASSCF calculations in the experimental geometry.

### Magnetic data

The measured magnetic susceptibility consists of the inherent temperature-dependent paramagnetic signal arising from the uncompensated spin and/or orbital angular momentum  $\chi_{\text{para}}$ , temperature-independent paramagnetism  $\chi_{\text{TIP}}$  arising from the close lying excited states, the underlying diamagnetism  $\chi_{\text{dia}}$  and the signal of the sample holder  $\chi_{\text{h}}$  (usually diamagnetic). Eventually some traces of the dioxygen or other paramagnetic impurities  $\chi_{\text{PI}}$  might be also present so that

$$\chi = \chi_{\text{para}} + \chi_{\text{TIP}} + \chi_{\text{dia}} + \chi_{\text{h}} + \chi_{\text{PI}} \quad (\text{Eq. 1})$$

On heating, the molar magnetic susceptibility of **1** decreases and passing through the zero it becomes almost constant (Fig. 4). The inherent paramagnetism of a hexacoordinate Co(III) complex possessing the ground electronic term <sup>1</sup>A<sub>1g</sub> is thought to be absent,  $\chi_{\text{para}} \sim 0$ . The low-temperature data refer to the traces of dioxygen that is present in the powder sample and obeys the Curie law. Also, the feature round 50 K is typical for the *solidus-solidus* phase transition of O<sub>2</sub>(s).



**Fig. 4.** Magnetic data for **1**. Left – molar magnetic susceptibility (SI units), right – dimensionless product function.

This signal escapes at the room temperature when  $\chi(300 \text{ K}) = -2.5 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$  (SI units) consisting only  $\chi = \chi_{\text{TIP}} + \chi_{\text{dia}} + \chi_{\text{h}}$ . The underlying diamagnetism can be calculated by means of the Pascal constants, however also a simple estimate using the molar mass  $M_r$  can be applied such as  $\chi_{\text{dia}} [10^{-12} \text{ m}^3 \text{ mol}^{-1}] = -5M_r [\text{g mol}^{-1}]$ ; this amounts to  $\chi_{\text{dia}} = -2.1 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ .

As the excited states of the same multiplicity are far away the ground state the temperature-independent paramagnetic term will be small. It can

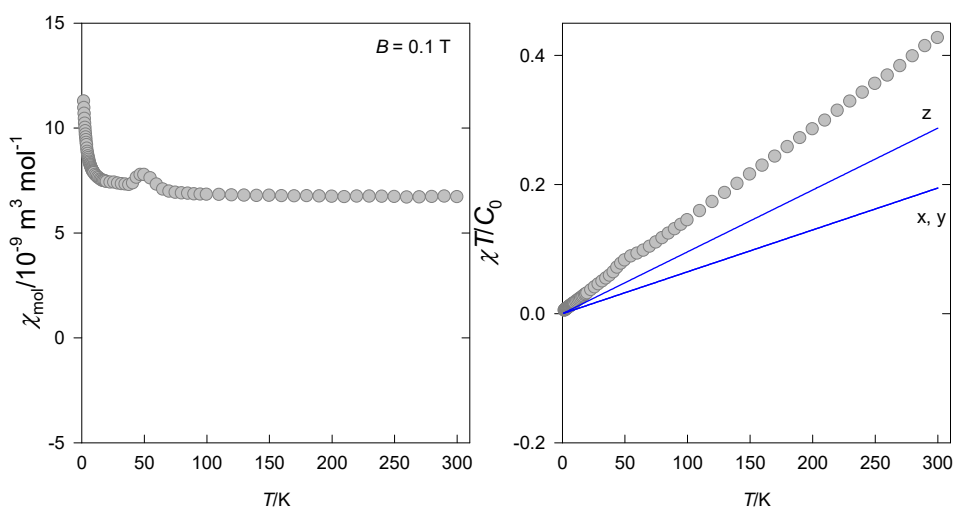
be hand-calculated by the spin-Hamiltonian formalism that offers the formula

$$\chi_{\text{TIP}} = -2N_A \mu_0 \mu_B^2 (\Lambda_{xx} + \Lambda_{yy} + \Lambda_{zz}) / 3 \quad (\text{Eq. 2})$$

containing the  $\Lambda$ -tensor components (restricted to the first excitation energy)

$$\Lambda_{aa} = - \frac{\langle \Psi_0 | \hat{L}_a | \Psi_1 \rangle^2}{E_1 - E_0} \quad (\text{Eq. 3})$$

The matrix element of the angular momentum operator for an octahedral Co(III) system is



**Fig. 5.** Magnetic data for **2**. Left – molar magnetic susceptibility (SI units), right – dimensionless product function. Lines – calculated with  $F_2 = 20\,000$  and  $F_4 = 10\,000 \text{ cm}^{-1}$ .

$\langle {}^1A_1 | \hat{L}_{x,y,z} | {}^1T_{1g} \rangle = 2$  and using the first singlet excitation energy  $\Delta E/hc = 21\ 000\ \text{cm}^{-1}$  one gets  $\chi_{\text{TIP}} = +2.4 \times 10^{-9}\ \text{m}^3\ \text{mol}^{-1}$ . The computer evaluation using the generalized crystal field theory yields  $\chi_{\text{TIP}} = +3.3 \times 10^{-9}\ \text{m}^3\ \text{mol}^{-1}$ .

The molar susceptibility for **2** at low temperature starts to decay on heating (Fig. 5), however it reaches almost constant value at the room temperature of  $\chi_{\text{mol}} = 6.7 \times 10^{-9}\ \text{m}^3\ \text{mol}^{-1}$  (SI units). This behaviour clearly deviates from the Curie law. The product function develops according to a straight line and this feature is a fingerprint of a considerable temperature-independent paramagnetism  $\chi_{\text{TIP}}$ . Small anomaly around 50 K is attributed to the *solidus-solidus* phase transition of dioxygen traces which are present in the powder sample. Using the crystal field poles  $F_2 = 20\ 000$  and  $F_4 = 10\ 000\ \text{cm}^{-1}$ , the GCFT calculations for a *quadro*-Ni(II) gave  $\chi_{\text{TIP}} = +3.1 \times 10^{-9}\ \text{m}^3\ \text{mol}^{-1}$ .

## Conclusions

Two novel low-spin Co(III) and Ni(II) complexes have been prepared and characterized by spectroscopic methods. X-ray structure analysis has shown that the complexes **1** and **2** possess with {CoS6} and {NiS4} chromophore, respectively. The study of bond angles and distances has revealed coordination polyhedron in octahedral (**1**) and square planar (**2**) arrangements. Magnetic studies confirmed a premise on diamagnetic behaviour of both complexes. Our primary goal was to prepare paramagnetic compounds of Co(II) and Ni(II). However, all attempts to prepare such compounds using the *xanth* ligand were unsuccessful.

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