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## Cobalt complexes supported by salicylychydrazono derivative ligands and various coordination solvents

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## ABSTRACT

We report the synthesis and molecular solid-state structures of five novel Co<sup>II</sup> and Co<sup>III</sup> mononuclear complexes supported by the 2-salicyloylhydrazono-1,3-dithiolane (**L1**) and 2-salicyloylhydrazono-1,3-dithiane (**L2**) ligands. Moreover, one novel diamagnetic  $\mu$ -oxo dinuclear Co<sup>III</sup> complex [Co<sup>III</sup><sub>2</sub>(**HL**)<sub>4</sub>( $\mu$ -O)<sub>2</sub>] supported by the ligand **L1** was stabilized and characterized. Crystal structure of the supporting ligand **L2** was also determined.

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### 1. Introduction

Control of magnetic coupling, in addition to the possibility of inducing a spin-state modification at the molecular scale, are among the most challenging themes in the field of molecular magnetism. Considering a large variety of magnetically interesting molecules [1], special attention has been paid in our lab to exchange coupled multinuclear transition metal paramagnetic complexes [2–4]. Systems presenting a lower nuclearity are of interest at least as versatile building blocks for cooperatively associated magnetic systems [5]. Due to the dependence of coupling pathways on the structure and symmetry of the organic ligands, dinuclear molecular systems offer interesting possibilities to tune metal-to-metal interactions by subtle structural changes within the organic periphery.

We earlier reported on an interesting dinuclear Mn<sup>III</sup> complex [Mn<sub>2</sub>(**HL**)<sub>4</sub>( $\mu$ -OCH<sub>3</sub>)<sub>2</sub>] (**H<sub>2</sub>L** is 2-salicyloylhydrazono-1,3-dithiolane) which was found to exhibit the largest *J* value (*J* = +19.7 cm<sup>-1</sup>) reported so far for a

Mn<sup>III</sup>–Mn<sup>III</sup> interaction [4]. On this basis, we have been working on slight modifications of its organic peripheral backbone as well as on using other metal centers. The peculiarity of the [Mn<sub>2</sub>(**HL**)<sub>4</sub>( $\mu$ -OCH<sub>3</sub>)<sub>2</sub>] solid-state structure arises from an unsymmetrical arrangement of the ligands, a feature most likely responsible for its ferromagnetic ground state. Recent work in our lab clearly established that the latter ferromagnetic Mn<sup>III</sup> complex only exists in the solid state [6]. A similar observation was made for the analogous Fe<sup>III</sup> complex supported by the same **H<sub>2</sub>L** ligand) that features, as expected, an antiferromagnetic exchange coupling behavior [7].

In an effort to gain more insight into the structural factors controlling and influencing the formation and the stabilization of both mono- and/or dinuclear complexes in the crystalline state (with possible impact on their magnetic behavior), the original **H<sub>2</sub>L** ligand (named **L1** in this work) was modified at specific positions (in this work the ligand 2-salicyloylhydrazono-1,3-dithiane – named **L2** – was synthesized). Moreover, the chemistry of other transition metals has been investigated systematically. In the present article, we report on the synthesis and structural characterization of novel Co<sup>II</sup> and Co<sup>III</sup> compounds supported by these two benzoic hydrazide ligands.

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## 2. Results and discussion

The initial task of the present work dealt with the synthesis and characterization of benzoic hydrazide ligand derivatives – 2-salicyloylhydrazono-1,3-dithiane (**L2**) – which are related to the original ligand we used (2-salicyloylhydrazono-1,3-dithiolane), yet are slightly modified (the five membered cycle – dithiolane, ligand **L1** – is replaced by a six member cycle – dithiane, ligand **L2**). Both ligands (**L1** and **L2**) were prepared according to literature procedures [8–10]. During the present work, the crystal structure of **L2** has been determined from single crystal X-ray diffraction. This result is briefly described hereafter.

### 2.1. Solid-state structures of the bidentate ligand **L2**

Crystal data and refinement details are gathered in Table 1 while selected bond lengths and angles are included in the figure caption (Fig. 1). The ligand **L2** crystallizes (colorless single crystals) in the monoclinic  $P2_1/c$  space group. In the solid state, the **L2** molecules are not planar (the angle between the phenol cycle and the average plan crossing the dithiane cycle is about  $30^\circ$  as clearly shown on the Fig. 1a), which contrasts with our previous observations in related ligands [6] (the ligand **L1** for instance). This rotation starts from the C6–C7 single bond (Fig. 1b), preventing the possible covering of both delocalized  $\pi$  electrons system (phenol group and hydrazine group) occurring in such molecule. This phenomenon could be a crucial parameter for metal complex stability as well as their physical properties (magnetic or photophysical for example). One classical

strong hydrogen bond is detected between N1 and O1 with the specific positions of both hydrogens bonded on N1 and O1 clearly depicted on Fig. 1b (dashed line).

### 2.2. Synthesis and structural characterization of $Co^{II}$ complexes

We then decided to explore the chemistry of  $Co^{II}$  complexes with the supported ligands **L1** and **L2**. Such complexes are paramagnetic compounds and thus potentially molecular magnets considering the polynuclear species. Moreover, comparison could be made with the previous  $Mn^{II}$  and  $Fe^{II}$  complexes previously obtained during our systematic work [7,8]. The synthesis and crystal structure of these complexes is described here.

Considering the new complexes synthesized in this present work, commercial crystalline  $CoCl_2$  was selected as main metal source. Direct reactions were successively carried out with **L1** and **L2** in different solvents (THF, DMF and Methanol).

The general way to obtain the  $Co^{II}$  complexes is described in Scheme 1. Three new compounds were obtained and characterized (see experimental section and Table 1) following this procedure: complex **1** [ $Co^{II}(\mathbf{L1})_2(\text{THF})_2$ ], complex **2** [ $Co^{II}(\mathbf{L1})_2(\text{DMF})_2$ ] and complex **3** [ $Co^{II}(\mathbf{L2})_2Cl_2$ ]. Their crystal structures were established from single crystal X-ray diffraction.

*Remark:* the charge (0 or  $-1$ ) of the ligands has been clearly identified by single crystal X-ray diffraction, i.e., presence (charge 0) or absence (charge  $-1$ ) of the hydrogen atom on N1 (Fig. 1b) as well as significant variation of  $d_{C-O}$  ( $\approx 1.245 \text{ \AA}$  for charge 0 and  $\approx 1.280 \text{ \AA}$  for

**Table 1**  
Crystal data and refinement details for **L2** and complexes 1, 2 and 3- $CH_2Cl_2$ .

Compound	Ligand <b>L2</b>	Complex <b>1</b>	Complex <b>2</b>	Complex <b>3-CH<sub>2</sub>Cl<sub>2</sub></b>
Formula	$C_{11}H_{12}N_2O_2S_2$	$C_{28}H_{34}CoN_4O_6S_4$	$C_{26}H_{32}CoN_6O_6S_4$	$C_{23}H_{26}Cl_4CoN_4O_4S_4$
Formula weight	268.35	709.76	711.75	751.45
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Crystal color	Colorless	Orange	Orange	Yellow
Crystal size	$0.14 \times 0.12 \times 0.10$	$0.14 \times 0.12 \times 0.10$	$0.14 \times 0.12 \times 0.10$	$0.14 \times 0.12 \times 0.10$
Space group	$P 2_1/c$	$P-1$	$C 2/c$	$P 2_1/c$
a (Å)	12.4480(5)	9.4170(2)	17.0940(6)	9.0089(2)
b (Å)	8.3280(4)	9.7000(4)	8.6200(2)	11.2411(4)
c (Å)	12.0840(6)	18.1100(7)	22.4670(8)	15.5647(6)
$\alpha$ (°)	90.00	99.3100(16)	90	90.00
$\beta$ (°)	105.880(3)	92.216(2)	108.272(12)	105.083(2)
$\gamma$ (°)	90.00	105.494(2)	90	90.00
V (Å <sup>3</sup> )	1204.90(10)	1567.30(9)	3143.6(3)	1521.93(9)
Z	4	2	4	2
Density (g.cm <sup>-3</sup> )	1.479	1.504	1.504	1.640
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.432	0.862	0.861	1.227
F(000)	560	738	1476	766
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Theta (min – max)	2.98–30.03	1.14–30.02	1.91–34.97	2.26–27.47
Dataset [h, k, l]	–17/17, –11/10, –16/14	–13/13, –13/13, –25/25	–27/13, –13/11, –36/36	–10/11, –14/13, –19/20
Tot., Uniq. Data, R(int)	8755, 3500, 0.0712	17410, 9070, 0.0521	13326, 6763, 0.0505	13746, 3495, 0.0393
Observed data (> 2 $\sigma$ (I))	3022	6319	5322	2739
Nreflections, Nparameters	3500, 154	9070, 399	6763, 200	3495, 196
R2, R1, wR2, wR1, Goof	0.0715, 0.0606, 0.1492, 0.1441, 1.112	0.0814, 0.0472, 0.1344, 0.1169, 1.039	0.0633, 0.0449, 0.1559, 0.1386, 1.068	0.0639, 0.0451, 0.1407, 0.1241, 1.086
Max. and Av. Shift/Error	0.001, 0.000	0.002, 0.000	0.001, 0.000	0.000, 0.000
Min. Max. Res. (e.Å <sup>-3</sup> )	–0.623, 0.755	–1.193, 0.473	–1.512, 1.524	–0.616, 0.853

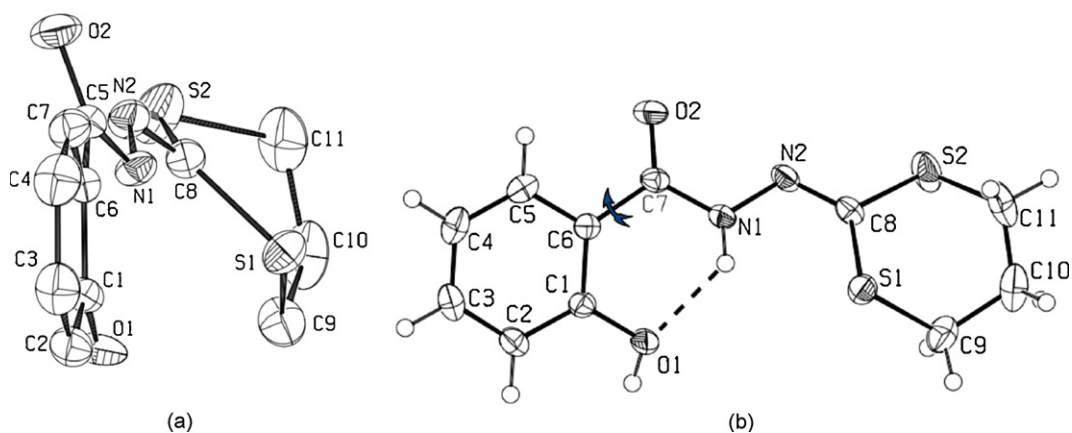


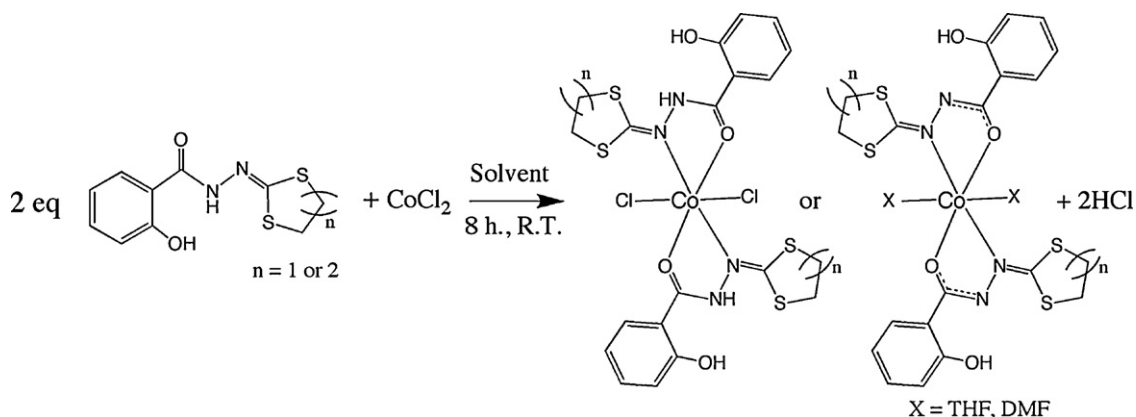
Fig. 1. a and b: Two perpendicular ORTEP views of the ligand **L2** with full labeling scheme. The ellipsoids enclose 50% of the electronic density. Selected distances (Å): C8–N2: 1.295(3); N2–N1: 1.393(3); N1–C7: 1.359(3); C7–O2: 1.221(3).

charge  $-1$ ) and significant variation of  $d_{C-N}$  ( $\approx 1.345$  Å for charge 0 and  $\approx 1.325$  Å for charge  $-1$ ). These phenomena have been confirmed for more than 12 other complexes synthesized and structurally characterized in our lab. These results will be published shortly. These observations indicate that the charge  $-1$  for deprotonated ligands is delocalized between O2 and N2 – Fig. 1b.

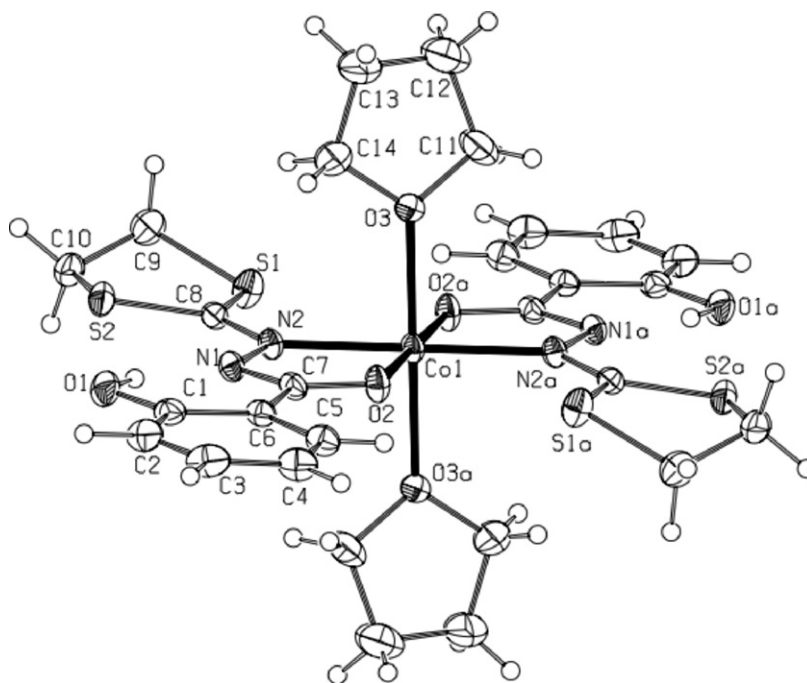
The orange complex **1** [ $\text{Co}^{\text{II}}(\mathbf{L1})_2(\text{THF})_2$ ] (Fig. 2) crystallizes in the triclinic centrosymmetric space group P-1. The asymmetric unit is constituted by two almost identical molecules of **1**. Only one of them is described here (see also the corresponding cif file for further information). The crystal structure clearly shows that the  $\text{Co}^{\text{II}}$  ion is surrounded by two **L1** (with the charge  $-1$ ) ligands in trans situation. The Fourier map differences (crystal structure refinement with Shelxl97) clearly shows the absence of hydrogen atoms on N1 (or N1a, Fig. 2), confirming the charge (1 for the ligand). The octahedral sphere is completed by two THF molecules, indicating the relative lability of the chloride atoms in such  $\text{Co}^{\text{II}}$  system. This lability is not observed in the case of  $\text{Fe}^{\text{II}}$  species [7,11]. All distances and angles (Fig. 2 caption) are coherent with such  $\text{Co}^{\text{II}}$  complex. Quite similar species were observed previously with  $\text{Mn}^{\text{II}}$  ion (complex **4b** in [8]).

The orange complex **2** [ $\text{Co}^{\text{II}}(\mathbf{L1})_2(\text{DMF})_2$ ] (Fig. 3) crystallizes in the monoclinic centrosymmetric space group C 2/c. Here again, the crystal structure shows that the  $\text{Co}^{\text{II}}$  ion is surrounded by two **L1** (with the charge (1) ligands in trans configuration). In this case, the octahedral sphere is completed by two DMF molecules. Selected distances are given in the caption of Fig. 3. Similar complexes have been already obtained with  $\text{Fe}^{\text{II}}$  ion<sup>11</sup>, and also with  $\text{Mn}^{\text{II}}$  but in this last case<sup>8</sup> a cis-configuration is observed for both ligands and the DMF molecules.

Several syntheses have been made, testing the reactivity of the ligand **L2** with  $\text{Co}^{\text{II}}$  salt, with various solvents. Only one new complex was stabilized and characterized with this ligand. The corresponding yellow complex [complex **3**- $\text{CH}_2\text{Cl}_2$ ,  $\text{Co}^{\text{II}}(\mathbf{L2})_2(\text{Cl})_2\text{-CH}_2\text{Cl}_2$ ] (Fig. 4) crystallizes in the monoclinic centrosymmetric space group P 2<sub>1</sub>/c. As often observed with such ligands, the crystal structure shows that the  $\text{Co}^{\text{II}}$  ion is surrounded by two neutral **L2** ligands in trans situation. The  $\text{Co}^{\text{II}}$  surrounding is (a deformed octahedral with typical distances and angles – selected distances are given in Fig. 4 caption) completed by two  $\text{Cl}^-$  in accordance with the charge +2 for the metal centre.



Scheme 1. General procedure for the synthesis of the  $\text{Co}^{\text{II}}$  complexes. Solvents are THF, DMF or  $\text{CH}_2\text{Cl}_2$ . ( $n = 1$  or  $2$  for **L1** and **L2** respectively).

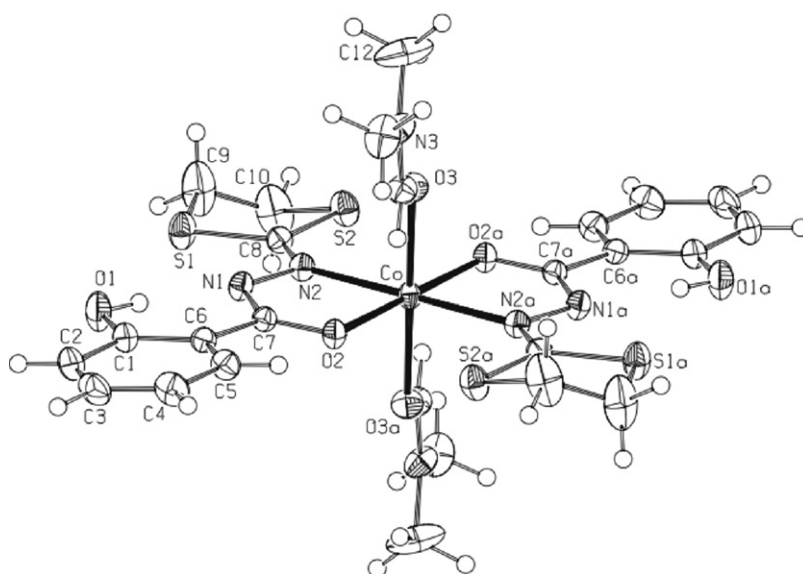


**Fig. 2.** ORTEP view of one molecule of the asymmetric unit of complex **1** with partial labeling scheme. The ellipsoids enclose 50% of the electronic density. Selected distances (Å): Co1–O2: 1.992(1); Co1–N2: 2.133(1); Co1–O3: 2.179(1); N2–N1: 1.412(2); O2–C7: 1.277(2). Symmetry codes for equivalent positions: *a*:  $-x+1, -y+1, -z+1$ .

### 2.3. Synthesis and structural characterization of Co<sup>III</sup> complexes

Considering the possibility of stabilizing Co<sup>III</sup> complexes with these supporting ligands, several tests were done. The target point was to obtain dinuclear Co<sup>III</sup> compounds. Firstly, the oxidation process of Co<sup>II</sup> into Co<sup>III</sup>

was driven in the presence of air, with a basic solution. With this approach, three new complexes (two mononuclear and one dinuclear) were obtained and structurally characterized. Direct reaction of the ligands with Co(OH)<sub>3</sub> freshly prepared (see below) is another way to synthesize these mononuclear complexes as well as the dinuclear compounds (with two equivalents of the ligand), as



**Fig. 3.** ORTEP view of complex **2** with partial labeling scheme. The ellipsoids enclose 50% of the electronic density. Selected distances (Å): Co–O2: 2.015(1); Co–N2: 2.134(1); Co–O3: 2.174(1); N2–N1: 1.404(2); O2–C7: 1.281(2). Symmetry codes for equivalent positions: *a*:  $-x+3/2, -y+1/2, -z+1$ .

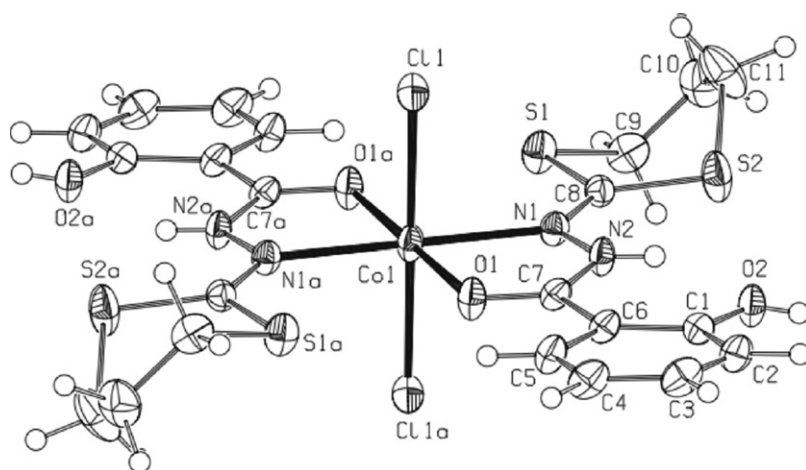
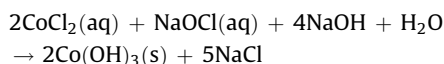


Fig. 4. ORTEP view of complex **3**-CH<sub>2</sub>Cl<sub>2</sub>, with partial labeling scheme. The solvent molecule was removed for clarity. The ellipsoids enclose 50% of the electronic density. Selected distances (Å): Co1–O1: 2.057(2); Co1–N1: 1.186(2); Co1–Cl1: 2.446(1); N2–N1: 1.384(3); O1–C7: 1.245(3). Symmetry codes for equivalent positions: *a*:  $-x+1, -y+1, -z$ .

described in the experimental section. The Co(OH)<sub>3</sub> reagent was prepared following this procedure:



The general way to obtain the Co<sup>III</sup> complexes is described in Scheme 2.

Both Co<sup>III</sup> mononuclear complexes **4**-CH<sub>2</sub>Cl<sub>2</sub> and **5**-CH<sub>2</sub>Cl<sub>2</sub> supported by **L1** and **L2** ligands respectively were obtained as single crystals suitable for X-ray diffraction. Their crystal structures are described hereafter.

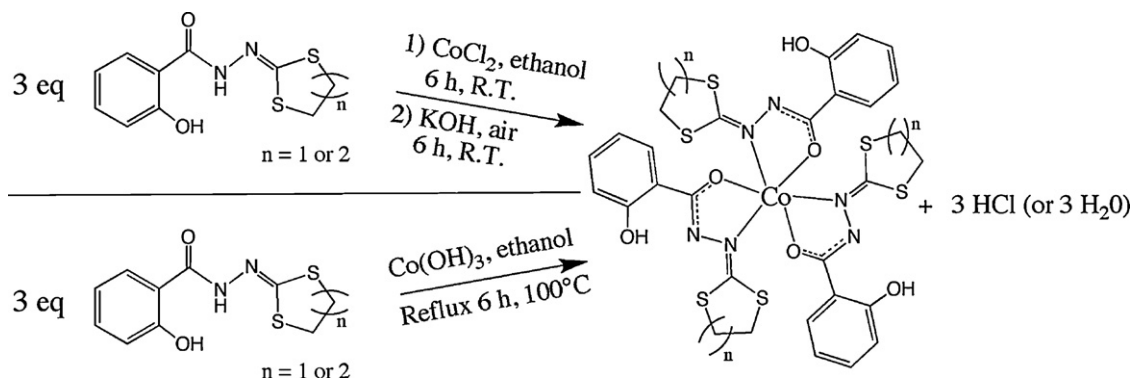
\* The red brown complex **4**-CH<sub>2</sub>Cl<sub>2</sub> [Co<sup>III</sup>(**L1**)<sub>3</sub>·CH<sub>2</sub>Cl<sub>2</sub>] (Fig. 5) crystallizes in the monoclinic centrosymmetric space group P 2<sub>1</sub>/a. The crystal structure clearly shows that the Co<sup>III</sup> ion is surrounded by three **L1** (with the charge –1) ligands inducing conformation chirality for each molecule. As clearly demonstrated in Fig. 5 (insert), two diastereoisomers constitutes the asymmetric unit with a total of four diastereoisomers in the unit cell. Selected distances are given in the Fig. 5 caption.

Many examples of such a coordination sphere around the Co<sup>III</sup> metal ion were reported [12] but only one example with hydrazine derivative ligand was already described; however, it involves a Mn<sup>III</sup> ion [5].

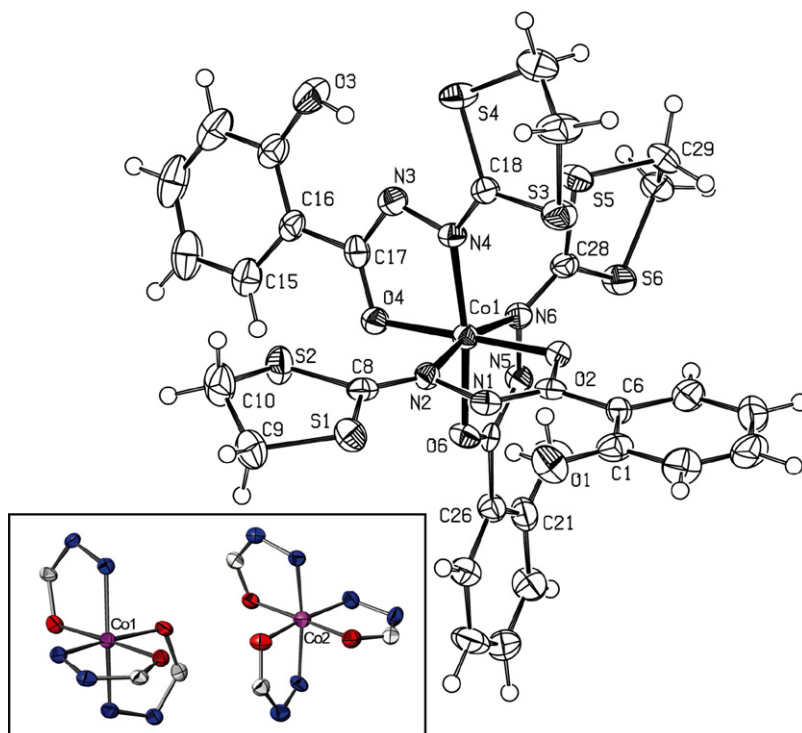
\* The red brown complex **5**-CH<sub>2</sub>Cl<sub>2</sub> [Co<sup>III</sup>(**L2**)<sub>3</sub>·CH<sub>2</sub>Cl<sub>2</sub>] (Fig. 6) crystallizes in the triclinic centrosymmetric space group P  $\bar{1}$ . The asymmetric unit contains only one isomer of the octahedral Co<sup>III</sup> complex supported by three **L2** ligands (with –1 charge), as clearly shown in Fig. 6. All distances are classical and very similar to those occurring in the complex **4**-CH<sub>2</sub>Cl<sub>2</sub>. Selected distances are gathered in the Fig. 6 caption. To our knowledge, it constitutes the first example of transition metal complex supported by the 2-salicyloylhydrazono-1,3-dithiane ligand (**L2**).

Considering the results obtained with mononuclear complexes, we tried to synthesize the  $\mu$ -methoxy dinuclear compounds by the way of direct synthesis of Co(OH)<sub>3</sub> with ligands **L1** and **L2**, respectively. Unfortunately, the numerous tests made with methanol as reagent as well as solvent did not give any result, probably due to the lack of solubility of Co(OH)<sub>3</sub> in methanol. On the other hand, syntheses carried out in ethanol as solvent (Scheme 3) allowed us to isolate a dinuclear complex with hydroxo bridges, but only with the ligand **L1**. Curiously, with the same synthetic procedure no reaction was observed with the ligand **L2**.

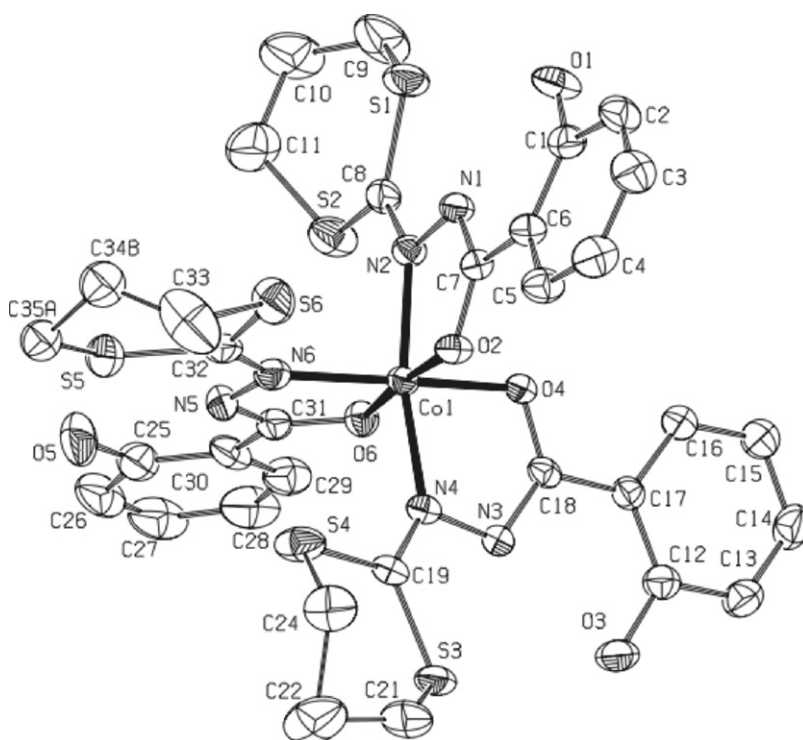
The dinuclear complex **6** were obtained as single crystals ready for X-ray diffraction by slow diffusion of



Scheme 2. The two different ways for the synthesis of the Co<sup>III</sup> complexes.

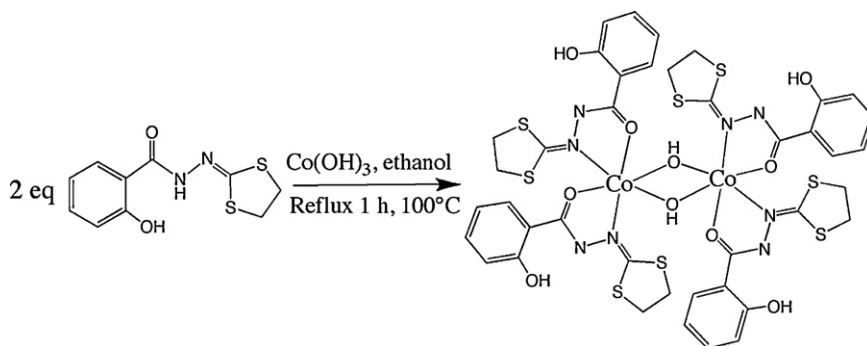


**Fig. 5.** ORTEP view of one molecule of the asymmetric unit of complex  $4\text{-CH}_2\text{Cl}_2$  with partial labeling scheme. The ellipsoids enclose 50% of the electronic density. Selected distances (Å): Co1-O2: 1.877(4); Co1-O4: 1.872(4); Co1-O6: 1.898(1); Co1-N2: 1.929(5); Co1-N4: 1.918(5); Co1-N6: 1.940(5). Insert: the two diastereoisomers of the asymmetric unit.



**Fig. 6.** ORTEP view of complex  $5\text{-CH}_2\text{Cl}_2$  with full labeling scheme. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms are not represented for clarity. Selected distances (Å): Co1-O2: 1.879(3); Co1-O4: 1.884(3); Co1-O6: 1.876(3); Co1-N2: 1.948(4); Co1-N4: 1.955(4); Co1-N6: 1.961(4).





Scheme 3. Synthesis of the  $\text{Co}^{\text{III}}$   $\mu$ -hydroxo dinuclear complex (**6**) supported by the ligand **L1**.

pentane in  $\text{CH}_2\text{Cl}_2$ . The corresponding crystal structure is described hereafter.

\* The black complex **6**: $5/2\text{CH}_2\text{Cl}_2$  [ $\text{Co}^{\text{III}}_2(\text{L1})_4(\text{OH})_2 \cdot 5/2\text{CH}_2\text{Cl}_2$ ] (Fig. 7) crystallizes in the triclinic centrosymmetric space group  $P\bar{1}$ . As clearly shown on Fig. 7, the molecular structure can be described as a 'symmetric'  $\mu$ -hydroxo bridged dinuclear complex in which both  $\text{Co}^{\text{III}}$  ions are in a slightly deformed octahedron (each one of them constituted by four oxygen atoms and two nitrogen atoms). The hydrogen atoms connected to the O9 and O10 oxygen atoms were found by Fourier transform, confirming that O9 and O10 are effectively hydroxy type bridges in this dinuclear compound. All distances and angles are classical with such a  $\text{Co}^{\text{III}}$  complex. The main particularity of this new complex is the 'symmetric' conformation observed: it is the first example with ligand **L1**. In fact, previous works involving dinuclear complexes with this ligand [5,7,13] always reveal a asymmetric configuration

for both metal ions,  $\text{Mn}^{\text{III}}$  or  $\text{Fe}^{\text{III}}$ , supported by specific non classical  $\text{CH}\cdots\pi$  interactions between the dithiolane group and the phenol ring (see, for instance, Fig. 1 in [5]). Moreover, each one of the octahedral sites is strongly deformed in the asymmetric complexes, as clearly shown in the insert of Fig. 7. In the present  $\text{Co}^{\text{III}}$  dinuclear complex, no specific intramolecular  $\text{CH}\cdots\pi$  interaction has been detected. Only classical H-bonds occur between the OH group of the phenol rings and the hydrazine groups indicating the charge (1 for the four supported ligands).

#### 2.4. Concluding remarks

In this article, we have presented the results of  $\text{Co}^{\text{II}}$  and  $\text{Co}^{\text{III}}$  chemistry with the ligands 2-salicyloylhydrazono-1,3-dithiolane ligand (**L1**) and 2-salicyloylhydrazono-1,3-dithiane (**L2**). Thus, six new complexes were synthesized and structurally characterized. Both ligands considered in

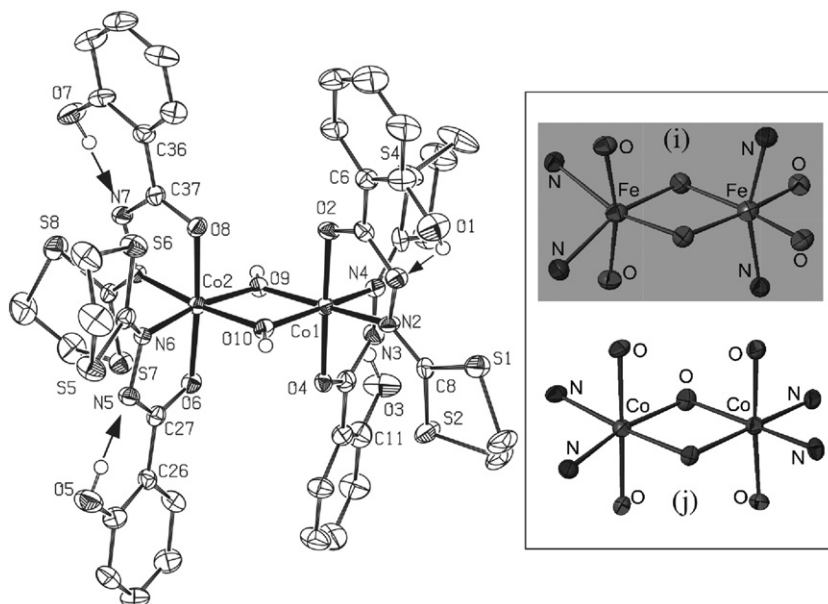


Fig. 7. Left: ORTEP view of complex **6**: $5/2\text{CH}_2\text{Cl}_2$  with partial labeling scheme. The ellipsoids enclose 50% of the electronic density. Arrows indicate the intramolecular hydrogen bonds. Selected distances (Å) and angles ( $^\circ$ ): Co1–O4: 1.878(4); Co1–O9: 1.887(4); Co1–O2: 1.893(4); Co1–O10: 1.920(5); Co1–N4: 1.926(6); Co1–N2: 1.935(5); Co1–Co2: 2.8695(12); Co2–O9: 1.879(4); Co2–O8: 1.885(5); Co2–O6: 1.889(5); Co2–N8: 1.916(5); Co2–O10: 1.934(4); Co2–N6: 1.939(6); Co1–O10–Co2: 96.2(2); Co2–O9–Co1: 99.3(2). Insert: cores of the dinuclear iron complex (i)<sup>13</sup> (asymmetric) and of the dinuclear cobalt complex (j) (symmetric, present work).

this work have very similar behavior with regard to the stabilization and crystal structures of the mononuclear compounds. On the other hand, only one dinuclear  $\text{Co}^{\text{III}}$  complex could be identified and structurally characterized with the supported ligand **L1**. In addition, this new dinuclear  $\mu$ -oxo dinuclear  $\text{Co}^{\text{III}}$  complex has, in contrast to the closely related compounds containing manganese and iron ions, a 'symmetrical' structure considering the configuration of the two ligands around each  $\text{Co}^{\text{III}}$  ion. Despite the fact that the complex is diamagnetic, this point is very interesting for our work within the framework of molecular magnetism. Indeed, for the strongly ferromagnetic compound containing manganese +III ion, we have shown that the origin of the strong ferromagnetic interaction is related to the perpendicularity of both  $d_{z^2}$  orbitals of the metal ion, i.e., related to the asymmetric situation in that complex. The challenge becomes, in that case, the possible control of the magnetic coupling by the synthesis, either of a symmetrical complex, awaited antiferromagnetic, or of asymmetrical complex awaited to be ferromagnetic. We currently work in that direction within our group.

### 3. Experimental

#### 3.1. General procedures

All reactions and manipulations, excepted for ligands **L1** and **L2**, were carried out under inert atmosphere of argon (AirLiquide, U-grade) using standard Schlenk tube techniques. Solvents were dried under nitrogen prior to use: tetrahydrofuran over sodium-benzophenone and dimethylformamide over sodium hydride. Elemental C, H, N, and S analyses were performed by the 'Service de Microanalyses' of Le Bel Institute and Charles Sadron Institute (ULP, Strasbourg, France). Infrared spectra were recorded as films on KBr disks, on a Perkin-Elmer 1600 series FTIR spectrometer. The  $^1\text{H}$  NMR spectra were recorded on a 300 MHz on a Bruker AVANCE 300 instrument.

#### 3.2. Synthesis

##### 3.2.1. General method for ligands

To a well-stirred solution of salicylhydrazide (9.13 g, 60 mmol) and NaOH (4.8 g, 120 mmol) in absolute ethanol (150 mL) at room temperature,  $\text{CS}_2$  (4.3 mL, 72 mmol) was added and the mixture was left under stirring overnight. Followed by the addition of 1,2 dibromoethane (5.2 mL, 60 mmol) (**L1**) or 1,3 dibromopropane (6.1 mL, 60 mmol) (**L2**). Stirring was continued for 8 h and the mixture was poured into ether. The resulting white precipitate was filtered and washed with ether. Recrystallization was performed from absolute ethanol.

##### 3.3. Ligand L1: 2-salicyloylhydrazono-1,3-dithiolane

Yield: 76% (11.58 g).

$^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ , 300K)  $\delta$ /ppm: 11.81 (br s, 1H, OH), 10.99 (br s, 1H, NH), 7.95–7.93 (d, 1H, Ar), 7.44–7.38 (t, 1H, Ar), 7.01–6.94 (m, 2H, Ar), 3.77–3.73 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{S}$ ), 3.62–3.58 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{S}$ ).

**Elemental analysis:** anal. Calc. for  $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_2\text{S}_2$ : C, 47.23; H, 3.96; N, 11.01; Found: C, 47.40; H, 4.10; N, 11.20.

IR  $\nu$  ( $\text{cm}^{-1}$ ): (OH) 3018  $\text{cm}^{-1}$ , (N–H) 2920  $\text{cm}^{-1}$ , (C=O) 1716  $\text{cm}^{-1}$ , (C=N) 1629  $\text{cm}^{-1}$ .

##### 3.4. Ligand L2: 2-salicyloylhydrazono-1,3-dithiane

Yield: 65% (10.45 g).

$^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ , 300K)  $\delta$ /ppm: 11.75 (br s, 1H, OH), 11.40 (br s, 1H, NH), 7.96–7.93 (d, 1H, Ar), 7.42–7.37 (t, 1H, Ar), 7–6.94 (m, 2H, Ar), 3.26–3.21 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$ ), 3.18–3.13 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$ ), 2.19–2.10 (m, 2H,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$ ).

**Elemental analysis:** anal. calc. for  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2\text{S}_2 + \text{H}_2\text{O}$ : C, 46.14; H, 4.93; N, 9.78; Found: C, 46.20; H, 4.98; N, 9.75.

IR  $\nu$  ( $\text{cm}^{-1}$ ): (OH) 3017  $\text{cm}^{-1}$ , (N–H) 2922  $\text{cm}^{-1}$ , (C=O) 1714  $\text{cm}^{-1}$ , (C=N) 1629  $\text{cm}^{-1}$ .

##### 3.5. General method for $\text{Co}^{\text{II}}$ complexes

To a solution of ligand (2 mmol) in THF, DMF or  $\text{CH}_2\text{Cl}_2$  ( $\approx$  35 mL), anhydrous  $\text{CoCl}_2$  (0.13 g, 1 mmol) was added. The mixture was stirred at room temperature overnight. The precipitate was filtered and washed with ether.

##### 3.6. Complex $\text{Co}^{\text{II}}(\text{L1})_2(\text{THF})_2$

X-ray quality crystals have been obtained by slow diffusion of pentane in THF.

Yield: 75% (0.42 g).

**Elemental analysis:** anal. calc. for  $\text{C}_{28}\text{H}_{34}\text{CoN}_4\text{O}_6\text{S}_4$ : C, 47.38; H, 4.83; N, 7.89; Found: C, 47.29; H, 4.57; N, 8.02.

**Mass spectroscopy (ESMS)  $m/z$ :** calc: 709.07 Found: (M + H), 708.13.

IR  $\nu$  ( $\text{cm}^{-1}$ ): (OH) 3026  $\text{cm}^{-1}$ , (C=N) 1631  $\text{cm}^{-1}$ .

##### 3.7. Complex $\text{Co}^{\text{II}}(\text{L1})_2(\text{DMF})_2$

X-ray quality crystals have been obtained by slow diffusion of pentane in DMF.

Yield: 71% (0.42 g).

**Elemental analysis:** anal. calc. for  $\text{C}_{26}\text{H}_{32}\text{CoN}_4\text{O}_6\text{S}_4$ : C, 43.87; H, 4.53; N, 11.81; Found: C, 43.39; H, 4.67; N, 11.85.

**Mass spectroscopy (ESMS)  $m/z$ :** calc: 711.06 Found: (M + H) 710.79.

IR  $\nu$  ( $\text{cm}^{-1}$ ): (OH) 3025  $\text{cm}^{-1}$ , (C=N) 1625  $\text{cm}^{-1}$ .

##### 3.8. Complex $\text{Co}^{\text{II}}(\text{L2})_2\text{Cl}_2$

X-ray quality crystals have been obtained by slow diffusion of pentane in  $\text{CH}_2\text{Cl}_2$ .

Yield: 67% (0.40 g).

**Elemental analysis:** anal. calc. for  $\text{C}_{22}\text{H}_{24}\text{CoCl}_2\text{N}_4\text{O}_4\text{S}_4$ : C, 39.64; H, 3.63; N, 8.41; Found: C, 40.70; H, 3.59; N, 9.27.

**Mass spectroscopy (ESMS)  $m/z$ :** calc: 664.94 Found: (M + H) 663.79.

IR  $\nu$  ( $\text{cm}^{-1}$ ): (OH) 3023  $\text{cm}^{-1}$ , (C=N) 1624  $\text{cm}^{-1}$ .

##### 4. General method for $\text{Co}^{\text{III}}$ complexes

**Method 1:** To a solution of ligand (3 mmol) in ethanol (30 mL), was added anhydrous  $\text{CoCl}_2$  (0.13 g, 1 mmol). The



mixture was stirred at room temperature overnight followed by the addition of KOH (0.17 g, 3 mmol). The solvent was removed under vacuum and the complex was extracted with dichloromethane.

**Method 2:** A solution of ligand (3 mmol) and  $\text{Co}(\text{OH})_3$  (0.11 g, 1 mmol) in ethanol (30 ml) was heated to 373K (100 °C) over 6 h. The solvents were removed under vacuum and the complex was extracted with dichloromethane.

#### 4.1. Complex $\text{Co}^{\text{III}}(\text{L1})_3$

X-ray quality crystals (red brown) were obtained by slow diffusion of pentane in  $\text{CH}_2\text{Cl}_2$ .

Yield: 46% (0.38 g) method 1, 70% (0.57 g) method 2.

$^1\text{H NMR}$  (300 MHz,  $\text{DMSO}-d_6$ , 300K)  $\delta/\text{ppm}$ : 11.14 (br s, 3H, OH), 8.14–8.02 (d, 3H, Ar), 7.35–7.26 (m, 3H, Ar), 6.97–6.81 (m, 6H, Ar), 3.73–3.36 (m, 12H,  $\text{SCH}_2\text{CH}_2\text{S}$ ).

**Elemental analysis:** anal. calc. for  $\text{C}_{30}\text{H}_{27}\text{CoN}_6\text{O}_6\text{S}_6$ : C, 44.00; H, 3.32; N, 10.26; Found: C, 44.15; H, 3.35; N, 10.39.

**Mass spectroscopy (ESMS)  $m/z$ :** calc: 817.965 Found: (M + H) 818.972.

$\text{IR } \nu$  ( $\text{cm}^{-1}$ ): (OH) 3028  $\text{cm}^{-1}$ , (C=N) 1638  $\text{cm}^{-1}$ .

#### 4.2. Complex $\text{Co}^{\text{III}}(\text{L2})_3$

X-ray quality crystals (red brown) were obtained by slow diffusion of pentane in  $\text{CH}_2\text{Cl}_2$ .

Yield: 39% (0.34 g) method 1, 66% (0.57 g) method 2.

$^1\text{H NMR}$  (300 MHz,  $\text{DMSO}-d_6$ , 300K)  $\delta/\text{ppm}$ : 11.07 (br s, 3H, OH), 8.13–8.02 (d, 3H, Ar), 7.35–7.25 (m, 3H, Ar), 6.96–6.79 (m, 6H, Ar), 3.21–2.02 (m, 18H,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$ ).

**Elemental analysis:** anal. Calc. for  $\text{C}_{33}\text{H}_{33}\text{CoN}_6\text{O}_6\text{S}_6$ : C, 46.04; H, 3.86; N, 9.76; Found: C, 45.98; H, 3.91; N, 9.69.

**Mass spectroscopy (ESMS)  $m/z$ :** calc: 860.012 Found: (M + H) 860.023.

$\text{IR } \nu$  ( $\text{cm}^{-1}$ ): (OH) 3036  $\text{cm}^{-1}$ , (C=N) 1640  $\text{cm}^{-1}$ .

#### 4.3. Complex $\text{Co}^{\text{III}}_2(\text{L1})_4(\mu\text{-OH})_2$

A solution of 2-salicyloylhydrazono-1,3-dithiolane (0.51 g, 0.2 mmol) and  $\text{Co}(\text{OH})_3$  (0.11 g, 0.1 mmol) in absolute ethanol (60 ml) was heated to 373K (100 °C) over 1 h and then the solution was dry under vacuum. The complex was extracted with dichloromethane and the resulting solution was dry under vacuum to obtain the complex.

X-ray quality crystals (black) have been obtained by slow diffusion of pentane in  $\text{CH}_2\text{Cl}_2$ .

Yield: 21% (0.25 g).

$^1\text{H NMR}$  (300 MHz,  $\text{DMSO}-d_6$ , 300K)  $\delta/\text{ppm}$ : 11.31 (br s, 4H, OH), 8.20–8.06 (m, 4H, Ar), 7.48–7.33 (m, 4H, Ar), 7.05–6.89 (m, 8H, Ar), 3.81–3.42 (m, 16H,  $\text{SCH}_2\text{CH}_2\text{S}$ ).

**Elemental analysis:** anal. calc. for  $\text{C}_{40}\text{H}_{38}\text{Co}_2\text{N}_8\text{O}_{10}\text{S}_8$ : C, 41.23; H, 3.29; N, 9.62; Found: C, 41.12; H, 3.10; N, 9.73.

**Mass spectroscopy (ESMS)  $m/z$ :** Calc: 1163.914; Found: (M + Na): 1186.903.

#### 4.4. Single crystal X-ray determination

Single crystals of ligand **L2**, complexes **1**, **2**, **3**· $\text{CH}_2\text{Cl}_2$ , **4**· $\text{CH}_2\text{Cl}_2$ , **5**· $\text{CH}_2\text{Cl}_2$  and **6**· $5/2\text{CH}_2\text{Cl}_2$  were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo  $\text{K}\alpha$   $\lambda = 0.71073$  Å). The complete conditions of data collection

**Table 2**

Crystal data and refinement details for **L2** and complexes **4**· $\text{CH}_2\text{Cl}_2$ , **5** and **6**· $5/2\text{CH}_2\text{Cl}_2$ .

Compound	Complex <b>4</b> · $\text{CH}_2\text{Cl}_2$	Complex <b>5</b> · $\text{CH}_2\text{Cl}_2$	Complex <b>6</b> · $5/2\text{CH}_2\text{Cl}_2$
Formula	$\text{C}_{31}\text{H}_{29}\text{Cl}_2\text{CoN}_6\text{O}_6\text{S}_6$	$\text{C}_{34}\text{H}_{35}\text{Cl}_2\text{CoN}_6\text{O}_6\text{S}_6$	$\text{C}_{42.5}\text{H}_{43}\text{Cl}_5\text{Co}_2\text{N}_8\text{O}_{10}\text{S}_8$
Formula weight	903.79	945.87	1377.44
Crystal system	Monoclinic	Triclinic	Triclinic
Crystal color	Red brown	Red brown	Black
Crystal size	0.20 × 0.10 × 0.10	0.15 × 0.12 × 0.10	0.10 × 0.10 × 0.10
Space group	P 2 <sub>1</sub> /a	P-1	P-1
a (Å)	17.862(5)	10.1690(3)	14.4720(5)
b (Å)	20.055(9)	11.9820(4)	14.8090(8)
c (Å)	22.136(7)	17.1820(7)	15.3940(7)
$\alpha$ (°)	90.00	72.475(2)	61.840(2)
$\beta$ (°)	103.06	88.260(2)	77.604(3)
$\gamma$ (°)	90.00	89.590(2)	70.858(3)
V (Å <sup>3</sup> )	7725(5)	1995.45(12)	2740.7(2)
Z	8	2	2
Density ( $\text{g}\cdot\text{cm}^{-3}$ )	1.554	1.574	1.669
$\mu$ (Mo $\text{K}\alpha$ ) ( $\text{mm}^{-1}$ )	0.957	0.930	1.216
F(000)	3696	972	1402
Data collection			
Temperature (K)	173(2)	173(2)	173(2)
Theta (min – max)	1.39–30.03	1.24–27.50	1.49–27.49
Dataset [h, k, l]	–25/24, 0/28, 0/31	–13/13, –15/15, –22/19	–18/18, –16/19, 0/19
Tot., Uniq. Data, R(int)	69715, 22568, 0.0000	19381, 9140, 0.0626	15257, 12489, 0.0000
Observed data (> 2 $\sigma$ (I))	6808	6541	6491
Nreflections, Nparameters	22568, 937	9140, 512	12489, 675
R2, R1, wR2, wR1, Goof	0.2554, 0.0873, 0.2148, 0.1725, 0.841	0.1067, 0.0746, 0.2127, 0.1869, 1.140	0.1622, 0.0799, 0.1984, 0.1507, 0.987
Max. and Av. Shift/Error	0.001, 0.000	0.000, 0.000	0.000, 0.000
Min, Max. Res. ( $\text{e}\cdot\text{Å}^{-3}$ )	–1.046, 1.528	–0.972, 2.424	–1.306, 1.714

(Denzo software) [14] and structure refinements are given in Tables 1 and 2. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods and refined against  $F^2$  using the SHELXL97 software [15]. The absorption was non-corrected.

All non-hydrogen atoms (excepted for CH<sub>2</sub>Cl<sub>2</sub> in **6-5**/2CH<sub>2</sub>Cl<sub>2</sub>) were refined anisotropically and hydrogen atoms were introduced as fixed contribution (SHELXL97) except for all hydrogen atoms of the ligand **L2** and for the hydrogen atom of the hydroxyl group for all complexes (found by Fourier differences).

Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication no. CCDC 742826 to CCDC 748332. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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