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# Molecular Tristability of $Co^{II}$ (salen)-based (salen = *N*,*N*'-ethylenebis(salicylideniminato) Compounds

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#### Abstract

The magnetic behaviors of Co(II) complexes of *N*,*N*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato, *N*,*N*-bis(3-chlorosalicylidene)-1,2-cyclohexanediaminato, *N*,*N*-bis(3,5-dichlorosalicylidene)-1,2-cyclohexanediaminato, (3-nitrosalicylidene)-1,2cyclohexanediaminato, *N*,*N*-bis(3,5-dinitrosalicylidene)-1,2-cyclohexanediaminato, and *N*,*N*-diaminomaleonitrilebis(salicylideniminato) were studied to identify the presence molecular tristability that is observed for the parent Co<sup>II</sup>salen (salen = ethylenebis(salicylideniminato)). *N*,*N*-bis(3,5-dinitrosalicylidene)-1,2-cyclohexanediaminato(2-)cobalt(II) exhibited tristable behavior similar to Co<sup>II</sup>salen, and it is anticipated to have a dimeric structure.

#### Keywords: Tristability; Co Compounds

#### 1. Introduction

Molecule-based electronics has received a great deal of interest due to the potential to overcome the current limits of silicon-based circuits [1]. Bistable molecule-based materials, in particular, have applications as vital components in sensors, switches, actuators, and information storage [2]. Molecular bistability refers to the existence of two stable states one within an environment and the other within another environment [2b]. Technologically important stimuli include electric fields, temperature, pressure, and light. Phenomena identified as initiating a reversible transition between states include spin-crossover [3], valence tautomerism [4], and photochromism [5]. Spin-crossover behavior occurs when the electronic structure of a metal ion is changed from a low spin

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to high spin state by a small change in temperature, pressure, and/or light, and have been identified as suitable bistable materials [2b,e]. Likewise, valence tautomers exhibit spin-state changes resulting from an intramolecular oxidation-reduction and have also been explored as bistable materials [6].

Spin-crossover behavior has been observed for many materials including a family of cobalt ions coordinated to Schiff's bases based upon N,N-ethylenebis(salicylideniminato)cobalt(II), Co<sup>II</sup>salen.



We reinvestigated the magnetic behavior of the dimeric form of N,Nethylenebis(salicylideniminato)cobalt(II) (Co<sup>II</sup>salen) [7]. The structure of Co<sup>II</sup>(salen) has been well established [8], and it exists in both monomeric and dimeric forms (Fig. 1). Monomeric Co<sup>II</sup>(salen) has a distinct 4-coordinate Co<sup>II</sup> center and has  $C_{2v}$  symmetry [9], while the dimeric form, [Co<sup>II</sup>(salen)]<sub>2</sub>, has pentacoordinate Co<sup>II</sup> with the phenolic oxygen of the other Co<sup>II</sup>(salen) moiety occupying the axial position [10], and overall has  $C_i$ symmetry [11].



Fig. 1. Structure of monomeric (a) and dimeric (b) Co<sup>ll</sup>(salen) [Co: dark blue; N: light blue; O: red, C: black; H: white].

While monomeric Co<sup>II</sup>(salen) is paramagnetic,  $[Co(salen)]_2$  has a singlet (S = 0) ground state with a triplet (S = 1) excited state, and at higher temperature we observed population of a quartet state (S = 3/2) [7]. Hence,  $[Co(salen)]_2$  has three stable spin

sates, and is tristable. This is attributed its dimeric structure with both  $Co^{II}N_2O_3$  centers being five-coordinate. Tristable materials was could lead to exciting applications in the fields of molecule-based switches and memory storage materials.

To better understand the genesis of the magnetic behavior of  $[Co(salen)]_2$ , and to identify compounds that exhibit similar behavior as the dimeric structure was associated with this molecular tristability, several new salen-substituted Co(II) complexes were sought. As analogue dimers based on the parent salen compound have not been observed, 1,2-diaminocyclohexane and diaminomaleonitrile were focused on as Schiff base backbones as a means to encourage crystallization, as synthesis of these compounds is described [12,13]. Hence, to understand and control the tristability, the following Co<sup>ll</sup>salen-based compounds were sought: bis(3,5-di-*tert*-butylsalicylidene)-1,2cyclohexanediaminato(2-)cobalt(II)], 1, N,N-bis(3-chlorosalicylidene)-1,2-cyclohexane-2, *N*,*N*-bis(3,5-dichlorosalicylidene)-1,2-cyclohexanediaminato(2-)cobalt(II), 3. N, N-bis(3-nitrosalicylidene)-1,2-cyclohexanediaminato(2-)diaminato(2-)cobalt(II), cobalt(II), 4, N,N-bis(3,5-dinitrosalicylidene)-1,2-cyclohexanediaminato(2-)cobalt(II), 5, and N,N'-diaminomaleonitrilebis(salicylideniminato(2-)cobalt(II), 6, targeted for study.



#### 2. Experimental Section

**2.1. Synthesis.** Solvents used included methanol (MeOH), ethanol (EtOH), 1-propanol (*n*-PrOH) and water (H<sub>2</sub>O). The alcohols were dried and sparged with N<sub>2</sub> before use. Ethylenediamine was obtained from Sigma Aldrich and was purified by atmospheric distillation. 1,2-cyclohexanediamine was purchased from Acros Organics and distilled at

atmospheric pressure and stored away from light. Diaminomaleonitrile was purchased from Sigma Aldrich and used without further purification. Unsubstituted salicylaldehyde was purchased from Sigma Aldrich and dried by stirring over CaCO<sub>3</sub> and then purified by distillation under high vacuum on a Vigeraux column. 5-Chlorosalicylaldehyde (Alfa Aesar), 5-nitrosalicylaldehyde (Alfa Aesar), 3,5-dichlorosalicylaldehyde (Arcos Organics), 3,5-dinitrosalicylaldehyde (Avocado Research Chemicals Ltd.) and 3,5-di-*t*-butylsalicylaldehyde (Arcos Organics) were used without further purification. Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato(2-)cobalt(II)], **1**, was a gift from a colleague [14]. Co(OAc)<sub>2</sub>•4H<sub>2</sub>O was purchased from Baker Chemical Company and dehydrated by heating to 140 °C for several hours according to the method described by Tsurata and coworkers [13].

**2.2. Schiff Bases.** The Schiff bases were synthesized following the method outlined by Bailes and Calvin [12], with the substitution of MeOH, EtOH, or *n*-PrOH for the alcohol was made in some situations. Coordination of Co(II) to the Schiff bases was achieved following the general procedure used by Tsurata and coworkers [13]. Reaction times, temperatures, and solvents were also adjusted as needed.

**2.3. Physical Methods.** Infrared spectra ( $\pm$  1 cm<sup>-1</sup>) were taken using a Bruker Tensor 37 spectrometer equipped with a liquid N<sub>2</sub> cooled detector. NMR spectra were recorded on a 300 MHz Varian Unity 300 Spectrometer quipped with a Nalorac Quad-probe (<sup>1</sup>H/<sup>19</sup>F, <sup>13</sup>C/<sup>31</sup>P) or equivalent. Low to room temperature magnetic susceptibilities were measured in applied fields of 1000 Oe between 5 and 400 K on a Quantum Design (QD) Magnetic Properties Measurements System (MPMS) superconducting quantum interference device (SQUID) equipped with a reciprocating samples measurement system, low field option, and continuous low temperature control with enhanced thermometry features as previously described [15]. Samples were ground to a powder and loaded in gelatin capsules, sealed with grease. The diamagnetic corrections noted below. Images of structures generated using CrystalMaker<sup>®</sup>; CrystalMaker Software Ltd, Oxford, UK.

Thermogravimetric analysis (TGA) was conducted on a TGA 2050 TA instrument. The instrument was stored in a Vacuum Atmospheres DriLab glove box filled with nitrogen, though the samples tested were not expected to be noticeably air-sensitive. Typical runs were conducted from 25 to 400 °C. Differential scanning calorimetry (DSC) was conducted on a TA Instruments DSC 2910 Modulated DSC with MDSC Cell Heat Exchange Assembly. The experiment was run for one cycle from 20 to 400 °C at a rate of 2.5 °C/min. Data was analyzed with Universal Analysis (version 4.4) software.

**2.3.1.** *N*,*N*<sup>\*</sup>-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato(2-)cobalt(II) (1). The complex was received as a gift. IR (KBr; cm<sup>-1</sup>);  $v_{C-H}$  2952, 2867 cm<sup>-1</sup>,  $v_{C=N}$  1595 cm<sup>-1</sup>  $v_{C=C}$  1527, 1465 cm<sup>-1</sup>. Elemental Anal. Calcd (obsd) for C<sub>36</sub>H<sub>50</sub>CoN<sub>2</sub>O<sub>2</sub> (1): C 71.86 (71.67), H 8.68 (8.72), N 4.66 (4.72). The diamagnetic correction of -366 x 10<sup>-6</sup> emu/mol was used.

# **2.3.2.** *N*,*N*'-Bis(5-chlorosalicylidene)-1,2-cyclohexanediaminato(2-)cobalt(II) (2). The Schiff's base was formed by dissolving 2.0 g (12.8 mmol) 5-chlorosalicylaldehyde in MeOH, forming a yellow solution. The reactions were then heated to 60°C. Upon boiling, a solution of 729 mg (6.39 mmol) ( $\pm$ )-*trans*-1,2-cyclohexanediamine dissolved in 10 mL MeOH was added dropwise via syringe over the course of 10 min. A yellow precipitate formed almost immediately. The reaction was then stirred for ~2 hr, after which time the solution was cooled to room temperature. The yellow solid was collected on a frit, washed with cold EtOH, and dried in air. Yield: 1.78 g (71%)]; IR (KBr; cm<sup>-1</sup>); $\nu_{C-H} 2926$ , 2852, $\nu_{C=N} 1632$ , $\nu_{C=C} 1573$ , 1478.

Next, 111 mg (0.282 mmol) of the resulting Schiff's base ligand was suspended in EtOH, the reaction was then placed under nitrogen and heated to 60 °C with stirring. To the slurry, 50 mg (0.282 mmol) of cobalt(II) acetate was added as a solid. A red-brown solid resulted almost immediate and the slurry was stirred for an additional 2 hrs. The red-brown solid was then collected on a frit and washed with EtOH and dried under vacuum. Yield: 120 mg (95%); IR (KBr; cm<sup>-1</sup>);  $v_{C-H}$  2936, 2857,  $v_{C=N}$  1601,  $v_{C=C}$  1521, 1447. Elemental Anal. Calcd (obsd) for C<sub>20</sub>H<sub>16</sub>Cl<sub>2</sub>CoN<sub>2</sub>O<sub>2</sub> (**2**): C 53.84 (53.59), H 4.05 (4.01), N 6.28 (6.05).The diamagnetic correction of -242 x 10<sup>-6</sup> emu/mol was used.

**2.3.3.** *N*,*N*<sup>\*</sup>-Bis(3,5-dichlorosalicylidene)-1,2-cyclohexanediaminato(2-)cobalt(II) (3). 3,5-dichlorosalicylaldehyde (2.00 g, 10.5 mmol) was dissolved in EtOH, and to this an EtOH solution of 0.598 g (5.24 mmol) of 1,2-cyclohexanediamine was added dropwise, resulting in a yellow precipitate. The stirring solution was then heated to 60 °C for 30 min before being cooled to room temperature. The resulting precipitate was then collected on a frit, washed with cold EtOH and air dried. Yield: quantitative IR (KBr; cm<sup>-1</sup>);  $\nu_{C-H}$  2939, 2862,  $\nu_{C=N}$  1632,  $\nu_{C=C}$  1570, 1452.

Next 1.0 g (2.17 mmol) of the yellow precipitate was suspended in hot 10 mL of 1-propanol heated to 60 °C and 385 mg (2.17 mmol) of cobalt acetate was added. The reaction was stirred at 60 °C for 1 hr and a brown precipitate formed. After 1 hr, the reaction was cooled to room temperature, the precipitate filtered off, washed with 2-propanol, and dried under vacuum. The precipitate was sticky and clogged the frit so acetone was used to wash the product. [Yield: 950 mg (85%)] IR (KBr; cm<sup>-1</sup>);  $v_{C-H}$  2939, 2861 cm<sup>-1</sup>,  $v_{C=N}$  1600 cm<sup>-1</sup>,  $v_{C=C}$  1514, 1436 cm<sup>-1</sup>. Elemental Anal. Calcd (obsd) for C<sub>20</sub>H<sub>14</sub>Cl<sub>4</sub>CoN<sub>2</sub>O<sub>2</sub> (**3**): C 46.64 (46.74), H 2.74 (2.95), N 5.44 (5.42). The diamagnetic correction of -276 x 10<sup>-6</sup> emu/mol was used.

**2.3.4.** *N*,*N***-Bis(5-nitrosalicylidene)-1,2-cyclohexanediaminato(2-)cobalt(II) (4).** The Schiff's base was formed by dissolving 2.0 g (12 mmol) of 5-nitrosalicylaldehyde and 683 mg (5.98 mmol) of 1,2-cyclohexanediamine in 30 mL of EtOH, under an inert N<sub>2</sub> atmosphere, with stirring. The reaction was then heated to 60 °C and stirred for 2 hr, during which time a yellow-orange solid precipitated. After 2 hr the precipitate was the collected on a frit and air-dried. Yield: 2.1 g (85%); IR (KBr; cm<sup>-1</sup>);  $\nu_{C-H}$  3065, 2954, 2865,  $\nu_{C=N}$  1652,  $\nu_{C=C}$  1554,  $\nu_{N=O}$  1619, 1309.

Next, 117 mg (0.282 mmol) of yellow-orange Schiff's base precipitate was dissolved in EtOH and 50 mg (0.282 mmol) of Co(OAc)<sub>2</sub> was added. The solution stirred for 2 hr at 60°C. The resulting brown slurry was then cooled to room temperature and the solid was collected on a frit, washed with EtOH, and dried under vacuum. Yield: 115 mg (87%); IR (KBr; cm<sup>-1</sup>):  $\nu_{C-H}$  3065, 2938, 2864,  $\nu_{C=N}$  1599,  $\nu_{C=C}$  1498,  $\nu_{N=O}$  1543, 1317.

Elemental Anal. Calcd (obsd) for  $C_{20}H_{16}CoN_2O_6$  (**4**): C 51.41 (51.50), H 3.45 (3.60), N 11.9 (11.94). The diamagnetic correction of -231 x 10<sup>-6</sup> emu/mol was used.

**2.3.5.** *N*,*N*'-Bis(3,5-dinitrosalicylidene)-1,2-cyclohexanediaminato(2-)cobalt(II) (5). 500 mg (2.36 mmol) of 3,5-dinitrosalicylaldehyde was dissolved in 20 mL of EtOH, forming an orange solution. Next, 134 mg (1.17 mmol) of ( $\pm$ )-*trans*-1,2-cyclohexanediamine was solvated in 12 mL EtOH forming a clear, colorless solution. The salicylaldehyde solution was then place under a N<sub>2</sub> atmosphere and heated to reflux (~70 °C). The EtOH solution of diaminocyclohexane was then added dropwise to the refluxing solution over the course of 0.5 hr. Orange precipitate was seen to crash out of the solution near the end of addition. The slurry was stirred at reflux for an additional 90 min, and then cooled to room temperature. The precipitate was collected on a frit and washed with ethanol and ether, yielding a bright orange solid. Yield: 550 mg (94%); IR (KBr; cm<sup>-1</sup>);  $\nu_{C-H}$  3087, 2958, 2865,  $\nu_{C=N}$  1652,  $\nu_{C=N}$  1619,  $\nu_{N=O}$  1554, 1339.

Next, 200 mg (0.398 mmol) of the orange Schiff base was dissolved in 20 mL of *n*-PrOH. The resulting orange solution was then placed under a N<sub>2</sub> atmosphere heated to 60 °C. Co(OAc)<sub>2</sub>, 71 mg (0.398 mmol), was added as a solid, causing the orange solution to turn a dark red-brown color. The reaction was stirred at 60 °C for 1 hr. The reaction was then cooled to room temperature and filtered through a frit, collecting a brown solid, which was then washed with *n*-PrOH and dried under vacuum. No crystals suitable for crystal X-ray diffraction could be grown Yield: 207 mg (93%) IR (KBr; cm<sup>-1</sup>):  $v_{C-H}$  3079, 2942, 2862,  $v_{C=N}$  1599 cm<sup>-1</sup>,  $v_{C=C}$  1560,  $v_{N=O}$  1525, 1331. Elemental Anal. Calcd (obsd) for **5**: C 42.95 (43.10), H 2.88 (2.99), N 15.03 (14.88). The diamagnetic correction of -255 x 10<sup>-6</sup> emu/mol was used.

**2.3.6.** *N*,*N*-bis{[(2-hydroxyphenyl)methylene]amino}-2-butenedinitrilato(2-)cobalt(II) (6). To 1.01 g (9.34 mmol) of diaminomaleonitrile dissolved in 150 mL of hot MeOH and filtered to remove nonsolvated starting material. The solution was then placed in three-neck flask fitted with water condenser and heated to ~60 °C, and, 1.94 mL (18.2 mmol) of salicylaldehyde was added dropwise over the course of 15 min resulting in an orange precipitate. The reaction was then stirred for 2 hr before being

cooled in freezer. The solid was then filtered off and washed with cold H<sub>2</sub>O and MeOH. The dried solid was then recrystallized from boiling methanol giving a microcrystalline orange solid *N*,*N*-bis[[(2-hydroxyphenyl)methylene]amino]-2-butenedinitrile. Yield: 1.09 g (34%); IR (KBr; cm<sup>-1</sup>):  $v_{C-H}$  2963,  $v_{C=N}$  2243, 2207,  $v_{C=N}$  1624,  $v_{C=C}$  1606, 149.

A slurry of 0.72 g (2.28 mmol) of the orange solid was formed in 10 mL of ethanol heated to 60 °C. An excess of cobalt acetate tetrahydrate (0.71 g; 4.02 mmol) was dissolved in 5 mL of water and added dropwise over the course of 10 minutes, forming dark brown slurry. The reaction was then stirred at 60 °C overnight before being cooled to room temperature and filtered under reduced pressure. The resulting solid was dark purple and fibrous. The purple solid was collected on frit and washed with cold ethanol. The solid was recrystallized from hot toluene, without noticeable change in the color or texture. Yield: 0.25 g (29.4%); IR (KBr, cm<sup>-1</sup>)  $v_{C-H}$  2952,  $v_{C=N}$  2216,  $v_{C=N}$  1605,  $v_{C=C}$  1574, 1514. Elemental Anal. Calcd (obsd) for **6**•0.5(EtOH)•1.3H<sub>2</sub>O; C<sub>19</sub>H<sub>5.6</sub>CoO<sub>3</sub>N<sub>4</sub>: C 54.38 (54.54), H 3.75 (4.00), N 13.35 (13.51). The diamagnetic correction of -119 x 10<sup>-6</sup> emu/mol was used.

#### 3. Results and Discussion

The syntheses of all of the substituted-salen compounds were conducted by established reaction schemes [12,13]. Formation of the Schiff bases were established through diagnostic signals in the IR spectrum. The appearance of the bands around 1638 ± 14 cm<sup>-1</sup> in all of the compounds indicated the formation of the C=N bond from condensation of the amine with the aldehyde. The recorded values are in good agreement with values previously reported in the literature [16]. Additionally, the spectra were shown to all possess absorptions from 2940 to 2970 cm<sup>-1</sup>, >1620 cm<sup>-1</sup>, and 1500 to 1600 cm<sup>-1</sup>, consistent with alkenyl  $\nu_{C-H}$ , conjugated  $\nu_{C=N}$ , and aromatic  $\nu_{C=C}$  stretching, respectively.

Formation of the Co(II) complexes from the Schiff bases was more difficult to ascertain from the IR spectra, as little change in the mid-IR could be detected. There was a recognizable shift of  $\sim 20$  cm<sup>-1</sup> in the C=N after coordination of the metal ion. This was accompanied by an intense color change. Coordination of the metal site was also confirmed through elemental analysis and magnetic studies of the compounds. None of

the substituted Co<sup>II</sup>-salen compounds formed either single crystals suitable for single crystal X-ray diffraction or powder diffraction analysis to elucidate their structure.

#### 3.1. Magnetic Properties

The magnetic susceptibilities,  $\chi$ , for all compounds were measured between 5 and 300 K at an applied filed of 1000 Oe, and are reported as  $\chi T(T)$  and  $\chi^{-1}(T)$ . All compounds are paramagnetic and do not exhibit any evidence of magnetic ordering.

Of the compounds studied, only **5** exhibited magnetic data similar to that seen in dimeric Co(salen). Comparison of the  $\chi T(T)$  data of  $[Co(salen)]_2$  and **5** shows a strong correlation (Fig. 2).  $\chi T(T)$  is 0.48 emu•K/mol at 300 K, 6.7% higher than what seen in our studies of  $[Co(salen)]_2$  [7]. This is somewhat lower than observed in other studies, but it is in reasonable agreement with the value expect for S = 1/2, g = 2.2, system. Below 275 K the susceptibility continues to decrease slowly until it reaches a plateau at 180 K of ~0.42 emu•K/mol, 2.4% lower than  $[Co(salen)]_2$  at that temperature. The  $\chi T(T)$  continues to slowly decrease with decreasing temperature to 0.372 emu•K/mol at 50 K. Below 50 K,  $\chi T(T)$  decreases rapidly to 0.218 emu•K/mol at 5 K. This behavior reflects the singlet-triplet transition behavior seen in  $[Co(salen)]_2$  with increasing temperature.

A fit of  $\chi T(T)$  of **5** to the Bleaney-Bowers singlet-triplet expression (eq 1) (eq per Co ( $H = -2J\mathbf{S}_i \cdot \mathbf{S}_j$ ), with g = 2.10 and  $J/k_B = -7.5$  K. The lower *g*-value is thought to arise from less spin anisotropy. As with [Co(salen)]<sub>2</sub>, the model breaks down after the single-triplet plateau, ~180 K. This occurs 20 K lower in temperature that seen in [Co(salen)]<sub>2</sub>, indicating an earlier onset of the spin crossover region. Additionally,  $\chi T(T)$  also deviates from the Bleaney-Bowers expression at low temperature, below 18 K.

$$\chi T = \frac{Ng^2 \mu_{\rm B}^2}{k_{\rm B}(3 + e^{-2J/k_{\rm B}T})}$$
(1)

Above 180 K,  $\chi T(T)$  is seen to gradually increase to 0.55 emu•K/mol at 320 K, 23% of the maximum theoretical value. Above 320 K,  $\chi T(T)$  shows the rate of increasing  $\chi T$  increases again. This increase can be seen in the  $1/\chi(T)$  data and corresponds to the onset of gradual weight loss observed in a thermogravimetric analysis of the compound, indicating decomposition of **5** (Fig. S1). This is consistent

with decomposition seen in  $[Co(salen)]_2$ . The lower decomposition temperature is attributed to destabilization of the compound due to the effect of the strongly electron withdrawing nitro-groups. An overlay of the  $\chi T(T)$  plots of the two compounds indicates that substitution of the nitro groups effectively lower the energy of the triplet state; thus, enabling more population of it, and reducing the onset temperature for the spin-crossover region.



Fig. 2.  $\chi T(T)$  of [Co(salen)]<sub>2</sub> dimer (blue, x) and 5 (red,  $\Delta$ ). Solid line is a fit to eq. 1.

This behavior is seen to be in sharp contrast to the behavior seen in other functionalized Co(salen) derivatives. The magnetic data for **1**, **2**, and **4**, (Fig. **3**) exhibited temperature independent  $\chi T$  of 0.519, 0.797, and 0.781 emu•K/mol at 300 K, respectively. These values are much larger than the expected value of 0.375 emu•K/mol for isolated spins of Co<sup>II</sup> with S = 1/2 and g = 2.0. Similar high values are seen in a number of substituted Co<sup>II</sup> compounds [10,17]. In these cases the large susceptibilities the discrepancies are either attributed to spin orbit coupling of the Co<sup>II</sup> centers and the effects of the planar salen ligand. In all of these cases the susceptibility is seen to remain consistent until low temperature (< 10 K), where evidence of weak antiferromagnetic coupling is observed. The presence of weak antiferromagnetic

coupling is observed for other Co(salen) systems as has been fit to linear 1-D Ising and 1-D Heisenberg chains as well as dimeric models and may be indicated interaction between Co(salen) complexes, though the lack of structural determination precludes accurate assignment of this behavior [12]. The presence of dimers seems unlikely as tristability has been linked to Co<sup>II</sup>(salen), which possess a definite structure [6].

The magnetic behavior of **3** indicates a room temperature  $\chi T$  value of 0.776 emu•K/mol-Co, respectively. This value falls within the room temperature  $\chi T$  values observed for related Co(salen) systems. Again, the discrepancy between the observed value and the expected room temperature  $\chi T$  value for a Co<sup>II</sup> ion is attributed to spin orbit coupling. However, while the magnetic response is well-behaved at higher temperatures, as the sample is measured below 35 K, a sharp rise in  $\chi T(T)$  to a maximum of 7.92 emu•K/mol for **3**, indicated the presence of ferromagnetic coupling (Fig. **3**). A similar response was noted by Murray and coworkers for oxygenated species of Co(salen) [12]. A tetrameric model provided the best fit for Murray, but the lack of crystal structures makes the assignment of this behavior difficult.

In contrast to the behavior of the most compounds with cyclohexyl-backbones, the magnetic response of **6** was also seen to show tristability. The room temperature  $\chi T(T)$  value is 2.25 emu•K/mol, much higher than the value seen in the previous compounds, but similar to the theoretical value for to S = 3/2 spin sites seen in related compounds [18]. The susceptibility is also in good agreement with literature values (2.21 emu•K/mol) for compounds with *N*-bound groups [9], it is beyond that seen for previous compounds would be anticipated from isolated spin values. The susceptibility continues to decrease with the temperature at a rate of ~0.002 emu•K/mol/K until ~250 K where the value is 2.13 emu•K/mol. Below 250 K, the  $\chi T(T)$  rapidly decreases to 0.783 emu•K/mol at 100 K, and below 100 K the rate decreases. The susceptibility slowly decreases to 0.564 emu•K/mol at 10 K. Below 10 K, the  $\chi T(T)$  decreases more rapidly until at 5 K, and the susceptibility is as 0.507 emu•K/mol.



Fig. 3.  $\chi T(T)$  (blue) and  $1/\chi(T)$  (red) **1** ( $\circ$ ), **2** ( $\bullet$ ), **3** ( $\blacktriangle$ ), and **4** (x).

The  $\chi T(T)$  behavior deviated from that expected of tristable cobalt salen materials. The  $\chi T(T)$  at low temperature (20 - 100 K), arising from the excited triplet state, is roughly twice as large as that seen for [Co(salen)]<sub>2</sub> and **5**. It does closely correspond to the value observed for functionalized Co(Salen) compounds **1** and **3**, where the large value is attributed to spin-orbit coupling of the Co<sup>II</sup> sites. However, similarly large room temperature values have been observed for *N*-substituted salen dimers compounds as was attributed to interaction between the cobalt centers and the steric constraints of these complexes [9]. The increase in  $\chi T(T)$  is attributed to spin crossover behavior that occurs near 100 K, and is at a much lower temperature with respect to other tristable compounds.

The compound is thought to decompose over time, as is observed in the magnetic data. After heating **6** to 400 K the sample was cooled and the temperature dependent susceptibility was measured multiple times. On the second run,  $\chi T(T)$  was 2.38 emu•K/mol, a 5.8% increase over the initial value. The  $\chi T(T)$  decreased with temperature where the difference between the measurements continues to increase (Fig. 4). The  $\chi T(T)$  measured 2.28 emu•K/mol at 250 K, 0.953 emu•K/mol at 100 K and 0.846 emu•K/mol at 30 K where it was 7.04, 21.71, and 33.65% higher than the original

measurement, respectively. Below 30 K, the  $\chi T(T)$  is seen to begin increasing, to 1.13 emu•K/mol at 5 K, indicating a ferromagnetic coupling in this region. The origin of this ferromagnetic region is not currently known, though may indicate oxygen complexation as ferromagnetic coupling has been noted by Murray is some oxygen-bound species. Successive measurements indicated a continued rise in the  $\chi T(T)$  plot, possible indicated decomposition of the compound.



Fig. 4.  $\chi T(T)$  (blue) and  $1/\chi(T)$  (red) of **6**.

#### 4. Conclusion

A series of functionalized Co<sup>II</sup>salen complexes were investigated for the presence of molecular tristability as observed for the unsubstituted dimer,  $[Co^{II}salen]_2$ .<sup>7</sup> Among the compounds studied only **5** and **6** exhibited data suggestive of tristability. Tristability is thought to arise from close association between Co<sup>II</sup> centers, as seen in the inactive form of Co<sup>II</sup>salen. Correlation between the electron withdrawing strength of the substituent groups is suspected to play a role in dictating the magnetic behavior. The only cobalt salen compound with an electron donating group, **1**, showed the lowest room temperature  $\chi T$  value. As the electron-withdrawing groups, CI and NO<sub>2</sub>, are introduced at the 5' position on the aromatic rings for compounds **2** and **4**, the  $\chi T(T)$ 

increases, though no evidence of tristability is noted. Further introduction of the electron-withdrawing groups at the 3' position of the aromatic ring appears to increase interaction between Co(salen) compounds. In the tetrachloro derivative **3**, there appears evidence of ferromagnetic coupling at low temperature. The tetranitro derivative **4**, shows a reduced  $\chi T$ , attributed to antiferromagnetic coupling of two Co(salen) interacting as dimers. The appearance of this phenomenon in the **5** and its absence in **4** is attributed to the greater electron withdrawing nature of the nitro compound.

Quantification of electronegativity of functional groups has been more difficult than that of atoms. However, several studies [19] have indicated the nitro group to have group electronegativity of 4.83 (Pauling units), 1.67 units greater than the Cl. This combined electronegativity is thought to decrease electron density on the metal center, increasing its propensity to form dimers through association with atoms of adjacent compounds.

This may also explain the appearance of tristability in **6** as studies have indicated the CN group to an electronegativity of 3.84, above that seen in CI [19]. The greater susceptibility values seen for **6** are thought to arise from the inclusion of the diaminomaleonitrile compound as the backbone. This enforces a rigid planar structure arising from the conjugated  $\pi$ -systems. A study by Murray and coworkers on Co(II) Schiff base complexes noted a similar trend, where higher susceptibilities were noted for compounds with 1,2-diaminobenzene serving as the backbone over compounds with ethylenediamine backbones.

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SUPPORTING INFORMATION. The TGA trace for **5**, This material is available free of charge via the Internet.

**Supporting Information** 



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# toc Molecular Tristability of $Co^{II}$ (salen)-based (salen = N,N'-ethylenebis(salicylideniminato) Compounds

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