



Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Research articles

Synthesis, structural characterization, photo-physical and magnetic properties of cobalt salphen pseudo halide complexes showing meta-magnetic ordering

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ARTICLE INFO

Article history:

Received 31 July 2017

Received in revised form 26 October 2017

Accepted 9 November 2017

Available online xxx

Keywords:

2D coordination polymer

Schiff base complexes

Metamagnetism

Cobalt complexes

Solvo-thermal synthesis

ABSTRACT

The solvo-thermal syntheses of [(CoSalphen)₂Co(SCN)₂]_n (**1**), CoSalphen(NH₃)(N₃) (**2**), Na[Co^{III}salphen(N₃)₂](**3**), Na[Co^{III}salen(N₃)₂](**4**) and Co^{III}salen(NH₃)(N₃) (**5**) {salphen = *N,N'*-*o*-phenylene-bis(salicylideneimine)}

are reported. The structural studies using X-ray diffraction measurements revealed that **1** crystallizes in a monoclinic C2/c space group. Two cobalt (II) metal centers in penta-coordinated and octahedral local coordination environments are bridged via alternating O and μ_{1,3} SCN bridges resulting in a novel 2D layered coordination polymer. Compound **2** is a trivalent mononuclear cobalt azido complex with an octahedral coordination environment. The magnetic investigations of **1** revealed ferromagnetic coupling ($J = +49.1 \text{ cm}^{-1}$) and meta-magnetic ordering. Time resolved photoluminescence studies of the complexes showed excited state lifetimes of ($\tau_1 = 0.4675 \text{ ns}$, $\tau_2 = 5.23 \text{ ns}$) for **1** and ($\tau_1 = 0.5078 \text{ ns}$, $\tau_2 = 6.79 \text{ ns}$) for **2**.

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1. Introduction

The main approach to construct molecular magnetic materials is to employ short bridging ligands to connect paramagnetic metal ions forming coordination polymers with different nuclearity, dimensionality and properties [1–3]. The linear triatomic pseudo-halide ligands (SCN⁻, N₃⁻ and OCN⁻) are typically used to engender the structural diversity of such coordination polymers due to their versatile bridging nature with very wide variety of bridging modes and angles.[4–7] More importantly, the small size and the extended π orbitals of these anionic ligands provide very efficient pathways for magnetic coupling between metal centers that can be used to mediate both ferro (e.g. [Co(tppz)(NCS)(μ-1,3-NCS)]_n, [Co(NCS)₂(bpe)]_n) [8,9] or antiferromagnetic interactions (e.g. [Co(SCN)₂(tBuPy)₂]_n) [10] depending on the bridging mode as well as the local coordination environment of the bridged metal centers [11–14].

Magnetic ordering phenomena in such materials have been shown to crucially rely on single-ion anisotropy [15,16]. Thus, the careful design and geometrical control over the local coordination environments of metal ions has led to enhanced magnetic properties leading to the observation of magnetic blocking phenomena in metal complexes with lower nuclearity down to mononuclear species [17–19]. Such structural control in coordination polymers is achieved in the building block approach by using pre-designed precursors in the construction of magnetic materials [3,20]. The use of the building block approach based on different pseudo-halide bridges has led to several interesting results including the isolation of discrete molecules [21], 1D [2], 2D [10,22–27] and 3D materials showing magnetic ordering [22,27,28].

Thermal decomposition/solvo-thermal conditions have been used to engender higher dimensionality and transform discrete complexes into 2D coordination polymers exhibiting magnetic ordering [10,24,25,27]. Salen type metallo-ligands have been used as precursors in a modular approach towards the controlled construction of metal pseudo-halide materials. Several examples have been previously reported including mononuclear Na[Co^{III}salen(N₃)₂] [29], trinuclear complexes; [(M^IL)₂M^{II}X₂] complexes [M_I = Cu or Ni, M_{II} = Co^{II} or Mn^{II}, L = salpn and X = cyanate, thiocyanate or azide][30,31], polymeric {Na[Co^{III}salpn(μ_{1,1}N₃)₂]_n [32], and

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mixed valent $[\text{Co}^{\text{II}}(\mu\text{OAc})_2(\mu\text{salpn})_2\text{Co}^{\text{III}}(\mu\text{SCN})_2]$ [33]. Recently, S. Thakurta et al. reported an interesting 2D cobalt coordination polymer; $[(\text{MeOsalpn})\text{Co}^{\text{II}}(\text{NCS})_2]_n$ [22] formed from O and $\mu_{1,3}$ SCN bridged cobalt centers in two different coordination environments (octahedral and tetrahedral) resulting in the observation of AF coupling and meta-magnetic ordering.

In this vein, we report the reactions of salen-based metallo-ligands with cobalt pseudo-halides (SCN^- and N_3^-). The structure of resultant products; $(\text{CoSalphen})_2\text{Co}(\text{SCN})_2$ (**1**), $\text{CoSalphen}(\text{NH}_3)(\text{N}_3)$ (**2**), $\text{Na}[\text{Co}^{\text{III}}\text{salphen}(\text{N}_3)_2]$ (**3**), $\text{Na}[\text{Co}^{\text{III}}\text{sal-en}(\text{N}_3)_2]$ (**4**) and $\text{Co}^{\text{III}}\text{-salen}(\text{NH}_3)(\text{N}_3)$ (**5**) have been elucidated using X ray diffraction and spectroscopic measurements. The magnetic properties of **1** have been investigated revealing the presence of meta-magnetic ordering. A thermal decomposition route of the precursor $\text{Na}[\text{Co}^{\text{III}}\text{salphen}(\text{N}_3)_2]$ (**3**) is proposed for the formation of **2** based on detailed structural studies.

2. Experimental

2.1. Physical measurements

Infrared spectra were recorded as KBr pellets on a Bruker VERTEX 70 FTIR spectrometer. Magnetic measurements were made on crushed crystalline sample using a Quantum Design Physical Property Measurement System (PPMS) instrument. The temperature dependence of the magnetization in the range between 2 and 300 K was recorded. Powder X-ray diffraction (XRD) patterns were collected using Cu $K\alpha$ monochromatic radiation ($K = 1.54056$) at room temperature on a 202964 Panalytical Empyrean diffractometer. Single crystal X-ray diffraction (SC-XRD) were collected using a Bruker D8 QUEST instrument. The structure was solved and refined using the Bruker SHELXTL Software Package. The figures and pictures of the structure were drawn by using Diamond 3.2 Software package. Elemental analysis were made using VARIO EL III CHNS Element Analyzer, Time-resolved Photo-luminescence spectroscopy was made using Pico Quant PDL 800-D pulsed driver with Picosecond Pulsed Diode Laser Head with wavelength 440 nm and Time-Correlated Single Photon Counting detector by Micro Photon Devices (MPD). UV-Vis spectroscopy were measured on Agilent Cary 60 UV-Vis spectrophotometer.

2.2. Materials

Salphen and Salen Schiff bases were synthesized according to literature [34] form condensation of Salicylaldehyde with *O*-phenylene diamine or ethylene diamine. Cobalt(salphen) H_2O was synthesized according to literature [35]. $\text{Na}[\text{Co}^{\text{III}}\text{salen}(\text{N}_3)_2]$ (**4**) was synthesized following the reported procedure [29]. All other chemicals and solvents are of analytical grade.

2.2.1. Synthesis of $[(\text{CoSalphen})_2\text{Co}(\text{SCN})_2]_n$ (**1**)

The precursor $[\text{Co}(\text{salphen})]\text{H}_2\text{O}$ (0.391 gm, 1 mmol) was added to $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.291 gm, 1 mmol) and NH_4SCN (0.152 g, 2 mmol) in 100 mL absolute ethanol. The reaction mixture was transferred into a Teflon lined stainless steel autoclave of 150 mL volume allowing about 70% of the bomb filled. The reaction was heated for 18 h at 423 K (150 °C) then slowly cooled (0.3 °C/min) to room temperature. The crystalline product was filtered off, washed several times with ethanol then dried at 70 °C for 2 h. Yield: 20%, 0.1615 g. Anal. cal. for $\text{C}_{42}\text{H}_{28}\text{Co}_3\text{N}_6\text{O}_4\text{S}_2$, MW: 921.64. C, 54.73; H, 3.06; Co, 19.18; N, 9.12; O, 6.94; S, 6.96. Found C, 54.58; H, 2.89; N, 8.91.

IR (KBr, cm^{-1}): $m = 3778, 3422, 3051, 3011, 2926, 2606, 2307, 2126$ ($\nu_{\text{as}} \text{SCN}$), 2082 ($\nu_{\text{as}} \text{SCN}$), 1596 (C=N), $1528, 1453, 1434, 1298, 1183, 1138, 1033, 921, 853, 799, 745, 658, 614$ cm^{-1} .

2.2.2. Synthesis of $\text{CoSalphen}(\text{NH}_3)(\text{N}_3)$ (**2**)

The precursor $[\text{Co}(\text{salphen})]\text{H}_2\text{O}$ (0.391 gm, 1 mmol) was added to NaN_3 (0.152 g, 2 mmol). In 100 mL absolute ethanol and stirred for 1 h in open air at room temperature. The reaction mixture was transferred into a Teflon lined stainless steel autoclave of 150 mL volume allowing about 70% of the bomb filled. The reaction was heated for 18 h at 423 K (150 °C) then slowly cooled (0.3 °C/min) to room temperature. The crystalline product was filtered off, washed several times with ethanol then dried at 70 °C for 2 h. Yield: 36%. Anal.cal. for **2**: $\text{C}_{20}\text{H}_{17}\text{CoN}_6\text{O}_2$, MW: 432.32. C, 55.56; H, 3.96; Co, 13.63; N, 19.44; O, 7.40. Found C, 55.58; H, 3.89; N, 19.53.

IR (KBr, cm^{-1}): $m = 3799, 3411, 3017, 2945, 2018$ ($\nu_{\text{as}} \text{N}_3$), 1607 (C=N), $1524, 1446, 1434, 1326, 1189, 1144, 1030, 938, 853, 747, 694$ cm^{-1} .

2.2.3. Synthesis of $\text{Na}[\text{CoSalphen}(\text{N}_3)_2]$ (**3**)

The synthesis process is following the method reported by Mathias et al. [29]. 1 mmol (0.291 gm) of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 mL 1:1 methanol: acetone then added to 1 mmol of the Schiff base dissolved in 10 mL methanol. The mixed solution was stirred for 1 h. Then 3 mmol NaN_3 , 0.195 gm in 2 mL water were added to the previously prepared solution and mixed for 15 min at room temperature. The final solution was then filtered and the filtrate was kept for crystallization by slow evaporation of solvent at room temperature. Fine black crystals were collected after two days. Yield: 90%. Anal.cal. for **3**: $\text{C}_{21}\text{H}_{17}\text{CoN}_8\text{NaO}_2$, MW: 495.34. C, 50.92; H, 3.46; Co, 11.90; N, 22.62; Na, 4.64; O, 6.46.

IR (KBr, cm^{-1}): $m = 3420(\text{b}), 2944(\text{m}), 2408(\text{sh}), 2106(\text{sh}), 2022$ (s) ($\nu_{\text{as}} \text{N}_3$), $1611(\text{s})$ (C=N), $1531(\text{s}), 1471(\text{s}), 1447(\text{sh}), 1380(\text{s}), 1316(\text{m}), 1188(\text{m}), 1147(\text{sh}), 929(\text{w}), 750(\text{m}), 540(\text{w}), 468(\text{w})$ cm^{-1} .

2.2.4. Synthesis of $\text{CoSalen}(\text{NH}_3)(\text{N}_3)$ (**5**)

0.1 mmol, 0.0432 gm of Complex 4 was dissolved in 10 ml methanol and heated to 150 °C for 1 h. Then cooled gradually to room temperature and left for crystallization. Yield about 90%. Anal.cal. for **5**: $\text{C}_{17}\text{H}_{18}\text{CoN}_6\text{O}_2$, MW: 397.08. C, 51.39; H, 4.57; Co, 14.83; N, 21.15; O, 8.05.

IR (KBr, cm^{-1}): $m = 3454(\text{br}), 2943(\text{w}), 2050(\text{sh}), 2013(\text{s})$ ($\nu_{\text{as}} \text{N}_3$), $1693(\text{sh}), 1637(\text{s})$ (C=N), $1599(\text{s}), 1537(\text{m}), 1448(\text{s}), 1344(\text{m}), 1308(\text{m}), 1285(\text{m}), 1203(\text{w}), 1151(\text{m}), 1129(\text{m}), 1085$ (w), $901(\text{m}), 760(\text{s}), 478(\text{w})$ cm^{-1} .

3. Results and discussion

3.1. Syntheses and structural Characterization

The solvo-thermal reaction of the metallo-ligand CoSalphen with $\text{Co}(\text{SCN})_2$ formed in-situ from $\text{Co}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and NH_4SCN in absolute ethanol at 150 °C resulted in the 2D coordination polymer $[(\text{CoSalphen})_2\text{Co}(\text{SCN})_2]_n$ (**1**). Whereas the reaction with NaN_3 in the same conditions resulted in the mononuclear complex $\text{CoSalphen}(\text{N}_3)(\text{NH}_3)$ (**2**). Compound **1** is insoluble in most solvents but soluble in Dimethylformamide (DMF) and Dimethyl sulfoxide (DMSO) suggesting polymeric nature of the compound. In compound **1**, two cobalt (II) salphen metallo-ligand are bridged via phenolic oxygens to a cobalt (II) center forming cobalt (II) trinuclear moieties which are further connected to each other through $\mu_{1,3}$ SCN^- bridges forming all cobalt(II) 2D layers. Compound **2** is partially soluble in alcohols and very soluble in DMF and DMSO. Similar compounds in literature such as $\text{Na}[\text{Co}^{\text{III}}\text{salen}(\text{N}_3)_2]$ [29] and $\{\text{Na}[\text{Co}^{\text{III}}\text{salpn}(\mu_{1,1}\text{N}_3)_2]\}_n$ [32] suggest that compound **2** is presumably resulting from the thermal decomposition of the diazido precursor (Scheme 1).

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