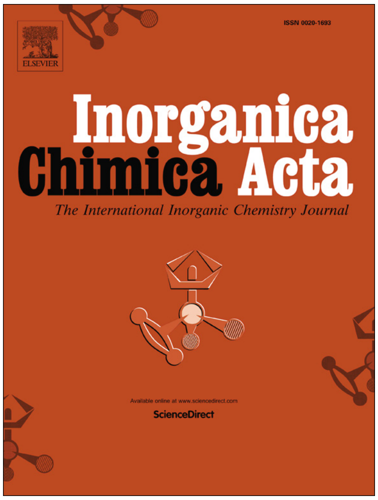

Research paper

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PII: S0020-1693(17)30248-7
DOI: http://dx.doi.org/10.1016/j.ica.2017.04.017
Reference: ICA 17522

To appear in: *Inorganica Chimica Acta*

Received Date: 20 February 2017
Revised Date: 7 April 2017
Accepted Date: 10 April 2017

Please cite this article as: N. Srivastav, R. Singh, V. Kaur, J. Wagler, E. Kroke, A stannatrane-like [4.4.4.0^{1,6}] heterotricyclic stannate anion possessing rhodanide antennae: A chromoreactand for Fe^{3+}, Cu^{2+} and Co^{2+} ions, *Inorganica Chimica Acta* (2017), doi: http://dx.doi.org/10.1016/j.ica.2017.04.017

A stannatrane-like [4.4.4.$0^{1,6}$] heterotricyclic stannate anion possessing rhodanide antennae: A chromoreactand for Fe^{3+}, Cu^{2+} and Co^{2+} ions

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Abstract

Exploration of an aminotrisphenol ligand (**H_3L**) to synthesise heterocyclic tin derivatives led to the unexpected formation of a stannatrane-like [4.4.4.$0^{1,6}$] heterotricyclic stannate anion $[LSnCl_2]^-$ (**1**). Further, its metathesis reaction with ammonium thiocyanate provided access to its thiocyanate derivative $[LSn(NCS)_2]^-$ (**2**), which proved to be a chromophoric probe. The characterization methods applied, such as elemental analysis, various spectroscopic methods (FT-IR, NMR (^1H, ^{13}C, ^{119}Sn), UV-Vis, Mass) and X-ray crystallography (for **2**) are in accord with the formation of these ionic compounds. The rhodanide functionalized stannatrane-like compound (**2**) was isolated as triethylammonium salt with distorted octahedral environment around Sn generated by the tripodal O_3N donor system and the N atoms of two *cis* configured thiocyanates. This particular organization of rhodanides imparted chelator and chromophoric character to **2** and enhanced its colorimetric and optical response towards some metal ions (such as Fe^{3+}, Cu^{2+} and Co^{2+} ions) as compared to the free tripodal ligand (**H_3L**) and ammonium thiocyanate. The role of **2** as a bidentate ligand for the chelation of metal ions may be responsible for the enhanced stability of metal complexes as well as the observed spectral behavior.

Keywords: Mannich base, aminotrisphenol, pseudo-stannatrane, thiocyanate, chemosensor, Fe^{3+}, Cu^{2+}, Co^{2+}.

1. Introduction

Fused heterotricyclic metalloorganics (termed as 'atranes') and their derivatives have gained interest due to their diverse reactivities and structural properties, especially when associated with ligands of varied steric and electronic factors [1-5]. In the past, fused heterotricyclic metalloorganics with symmetric [3.3.3.$0^{1,5}$] podand systems have been studied extensively [6-8] due to their distinct structural features, stability and wide spread applications in catalysis, sol-gel processes, cross-coupling and biological systems [9-12]. In these compounds, three heterocyclic rings form a 'propeller' like structure and the bridgehead positions are occupied by a central atom (transition metal or main group metal/metalloid) and nitrogen. Aminoalkanol and aminophenol derived tin compounds of this class are commonly termed as 'stannatranes' or 'pseudostannatranes' depending upon the tripodal ligating systems [13-15]. These are gaining immense interest due to their structural diversity which includes mono-, di-, tri-, tetra- (ladder like) and penta-nuclear oxo-clusters [13-18]. Generally, heterotricyclic organotin compounds are likely to associate to form oligomeric units in solid state due to the presence of lone pair donor atoms in their tricyclic ligating system and the unsaturated tin coordination sphere [14-16]. Generally speaking, the formation of oligomeric clusters in these compounds is a consequence of low steric protection induced by flexible arms $N(CH_2)_nO$ present in the tripodal ligating environment. Only those heterotricyclic tin compounds are monomeric with distorted trigonal bipyramidal units, which possess either the steric constraints on the ring skeleton or the bulky exocyclic substituent or lack lone pair donor groups in the ring skeleton [13,17-19]. Recently, a strategy to control the ligating environment for the isolation of oligomeric fused [3.3.3.$0^{1,5}$] heterotricycles has been reported by Zoller *et al.* [13,14].

In order to stabilize stannatrane moieties as monomeric units, we have chosen aminotrisphenolate ligands because of the structural rigidity offered by phenolic arms and achievement of favourable topological control [2]. They feature a central nitrogen atom (of the tripodal ligand) for the formation of a transannular bond with the central atom to generate a pseudo 3-fold symmetric environment resulting in a fused [4.4.4.$0^{1,6}$] heterotricycle [20-24]. In this ligand system, bulkiness of the ring skeleton caused by *ortho* and *para* substituted phenyl rings, can disfavour the interaction between two heterotricyclic molecules and thus support the formation of monomeric complexes. Numerous reports are available in literature on effective coordination of aminotrisphenolate ligating systems with transition metals and main group elements, which confirmed the formation of monomeric units (with exceptions of dimeric Al complexes and μ-oxo dimeric Ti complexes when the ligand bears less bulky substituents on the phenolate rings) [2, 25-27].

Aminotrisphenolate showed exclusive monomeric pseudo-atrane chemistry with silicon [28-32] and germanium [33] as they tend to form fused [4.4.4.$0^{1,6}$] heterotricycles with trigonal bipyramidal coordination sphere of the central atom (**Chart 1a** and **1b**). Silicon-trisphenolate compounds can be isolated in water-dichloromethane mixtures without undergoing hydrolysis because the rigid and bulky ligating system protects the central silicon from the attack of water molecules [28-32]. In addition to its tetradentate tripodal NO_3 coordination (as fully deprotonated L^{3-} ligand, aminotrisphenolate can be used as an O_3^- chelator, as was shown by the synthesis of a zwitterionic Sn(II) compound (**Chart 1c**), and in a Zr(IV) complex it was proven capable of acting as HL^{2-} ligand [34].

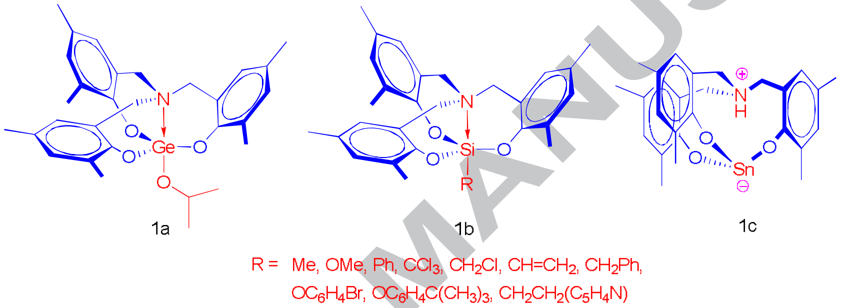


Chart 1. Pseudoatranes of Group 14 involving a tripodal aminotrisphenolate moiety.

Working on a similar type of ligating systems, recently we reported the formation of [4.4.3.$0^{1,6}$] pseudostannatranes with a semi-rigid aminobisphenolate ligand having one flexible ethanolate arm [15]. Interestingly, despite of steric protection induced by two substituted o-phenylene units in the fused [4.4.3.$0^{1,6}$] heterotricycle, one flexible arm provided an active site to extend the coordination sphere around Sn. Hence, fused [4.4.3.$0^{1,6}$] heterotricycles with hexacoordinate tin atoms were isolated.

Utilizing the stability effects offered by a trisphenolate ligating system (**H_3L**) and hexacoordination of tin, we report herein a triethylammonium salt of fused [4.4.4.$0^{1,6}$] heterotricyclic derivative of Sn possessing two exocyclic –NCS substituents. It was obtained in two steps; 1) formation of $Et_3NH[LSnCl_2]$ (**1**), and 2) derivatization to $Et_3NH[LSn(NCS)_2]$ (**2**). Single crystal X-ray diffraction studies of $Et_3NH[LSn(NCS)_2]$ revealed the formation of a salt with monomeric fused [4.4.4.$0^{1,6}$] heterotricyclic stannate anions. Because of steric constraints, two cis positions are occupied by –NCS groups as exocyclic substituents and the rest by the tripodal tetradentate ligating system. The presence of two cis-disposed –NCS groups imparts both chelating and chromogenic characteristics to $Et_3NH[LSn(NCS)_2]$.

Interestingly, solution of **2** becomes visible to the naked eye immediately on the addition of metal ions (such as Fe^{3+}, Cu^{2+} and Co^{2+} ions). Moreover, the colorimetric and optical response of this compound is enhanced over corresponding free ligand (**H_3L**), ammonium thiocyanate as well as combinations thereof. Hence, the compound may act as colorimetric and optical sensor for detecting the presence of these metal ions. Although, polydentate/supramolecular ligating systems have been widely used for sensing purposes, however, this is the first report on sensing metallic species utilizing trisphenolate based complex anions [35-37].

2. Experimental

2.1. Materials

Synthesis of all compounds was performed under a dry nitrogen atmosphere using Schlenk technique. Solvents were purchased commercially, dried before use and stored under nitrogen atmosphere. Triethylamine (CDH) was distilled over KOH pellets. Tin tetrachloride (Acros), hexamethylentetramine (Merck), 2,4-dimethylphenol (Merck), ammonium thiocyanate (Merck), ferric nitrate nonahydrate (Merck), copper nitrate trihydrate (Merck), cobalt nitrate hexahydrate (Merck), manganese acetate (Acros organics), cadmium chloride (CDH), chromium nitrate nonahydrate (Merck), lead nitrate (Fisher scientific), zinc nitrate hexahydrate (CDH) and nickel nitrate hexahydrate (CDH) were used as such without any purification.

2.2. Physical measurements

Infrared spectra were routinely obtained on Thermo scientific NICOLET IS50 FT-IR and Perkin Elmer RX-I FT-IR spectrophotometers. Mass spectral measurements (ESI source with capillary voltage 2500 V) were carried out on a VG Analytical (70-S) spectrometer. C, H, N elemental microanalyses were obtained on a FLASH-2000 organic elemental analyzer. The solution NMR spectra were recorded at 25 °C on a Bruker Avance II FT NMR (AL 400 MHz) spectrometer (^1H, ^{13}C, ^{119}Sn). Chemical shifts in ppm are reported relative to tetramethylsilane (TMS) for ^1H and ^{13}C or tetramethylstannane for ^{119}Sn. Single-crystal X-ray diffraction data were collected on a Stoe IPDS-2T diffractometer using Mo Kα radiation (λ 0.71073 Å). The structure was solved by direct methods (SHELXS-97) and refined with full-matrix least-squares method (refinement of F^2 against all reflections with SHELXL-97). Ultraviolet-visible (UV-vis) spectra were recorded using a Jasco V-530 UV-vis spectrophotometer.

2.3. Synthesis

2.3.1. Synthesis of the aminotrisphenol ligand $\boldsymbol{H_3L}$.

This ligand was synthesized following a method reported in literature [31]. Briefly, hexamethylenetetramine (3.80 g, 27.1 mmol) and 2,4-dimethylphenol (15.0 mL, 124 mmol) with a catalytic amount of *p*-toluenesulfonic acid hydrate (0.10 g) were heated in an oil bath at 110 °C for 20 h. Then, an additional quantity of 2,4-dimethylphenol (5.00 mL, 41.4 mmol) was added and heating was continued for a further period of 20 h. The resultant solid was recrystallized from acetone (100 mL). Yield 72 % (16.4 g, 39.0 mmol); m.p. 174-178 °C; FT-IR (cm^{-1}): 1153 (C–N), 1211 (C–O), 1482, 1609 (C=C), 2868, 2912, 3011(C–H), 3366, 3517 (–OH); ^1H NMR (400 MHz, DMSO): δ (ppm) 2.14 (s, 9H, Ar–CH_3^{7}), 2.18 (s, 9H, Ar–CH_3^{8}), 3.60 (s, 6H, NCH_2), 6.76 (s, 3H, H^5), 6.77 (s, 3H, H^3), 8.84 (br., 3H, OH).

*2.3.2. Synthesis of $Et_3NH[LSnCl_2]$ (**1**).*

Aminotrisphenol $\mathbf{H_3L}$ (1.00 g, 2.38 mmol) was dissolved in dry tetrahydrofuran (20 mL) in the presence of anhydrous triethylamine (1.01 mL, 7.16 mmol), and tin tetrachloride (0.28 mL, 2.38 mmol) was added to it drop wise with stirring. The contents were stirred for about 5 h at room temperature and then filtered to remove the precipitated triethylammonium chloride. The salt was washed with THF and from the filtrate the solvent was evaporated and the solid obtained was dried under vacuum. Yield (crude product): 96 % (1.63 g, 2.30 mmol); m.p.: 195-198 °C. FT-IR (cm^{-1}): 417 (Sn–N), 537 (Sn–O), 1159 (C–N), 1263 (C–O), 1478, 1605 (C=C), 2868, 2910, 2949, 2994 (C–H), 3101 (N-H). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.25 (t, $^3J(^1H\text{-}^1H)$ = 7 Hz, 9H, triethylammonium CH_3), 1.76 (s, 3H, Ar–CH_3^{16}), 1.95 (s, 6H, Ar–$CH_3^{7,25}$), 2.08 (s, 6H, Ar–$CH_3^{8,26}$), 2.13 (s, 3H, Ar–CH_3^{17}), 3.09 (q, $^3J(^1H\text{-}^1H)$ = 7 Hz, 6H, triethylammonium NCH_2), 3.16 (d, $^2J(^1H\text{-}^1H)$ = 11 Hz, 2H, $NCH_2^{9,27}$), 3.73 (br., 2H, NCH_2^{18}), 5.25 (d, $^2J(^1H\text{-}^1H)$ = 11 Hz, 2H, $NCH_2^{9',27'}$), 5.60 (s, 1H, H^{14}), 6.37 (s, 1H, H^{12}), 6.47 (s, 2H, $H^{5,23}$), 6.59 (s, 2H, $H^{3,21}$), 9.34 (br., 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 8.67 (triethylammonium CH_3), 16.61 (Ar–$CH_3^{7,16,25}$), 20.38 (Ar–$CH_3^{8,17,26}$), 46.32 (triethylammonium NCH_2), 55.77 ($NCH_2^{9,18,27}$), 116.58 ($C^{6,15,24}$), 126.60 ($C^{2,11,20}$), 129.27 ($C^{5,14,23}$), 129.75 ($C^{3,12,21}$), 133.93 ($C^{4,13,22}$), 151.17 ($C^{1,10,19}$). ^{119}Sn (149 MHz, $CDCl_3$): δ (ppm) -624. MS: m/z (relative abundance (%) assignment): 135 (14.84) $[C_9H_{11}O]^+$, 402 (92.20) $[M - Cl - OPh(CH_3)_2CH]^+$, 420 (72.06) $[L + H]^+$, 536 (100) $[M - 2Cl - (C_2H_5)_3NH]^+$, 554 (10.84) $[M + NH_3 - (C_2H_5)_3NH + H]^+$, 606 (4.04) $[M - (C_2H_5)_3NH]^+$. $C_{33}H_{46}Cl_2N_2O_3Sn$ (708.35): calcd. C 55.95, H 6.55, N 3.95; found C 55.80, H 6.55, N 4.06.

*2.3.3. Synthesis of $Et_3NH[LSn(NCS)_2]$ (**2**).*

A solution of compound **1** (1.00 g, 1.41 mmol) and NH_4SCN (0.21 g, 2.82 mmol) in dry acetonitrile was stirred overnight. The resulting solution was filtered and the solvent was removed under vacuum to obtain solid. The product was recrystallized from dichloromethane-hexane to get crystals for single crystal X-ray diffraction studies. Yield (crude product) 95 % (1.01 g, 1.34 mmol), m.p.: 225-228 °C. FT-IR (cm^{-1}): 418 (Sn–N), 538 (Sn–O), 1160 (C–N), 1241 (C–O), 1476, 1613 (C=C), 2061, 2005, 1978 (–NCS), 2855, 2921, 2990 (C–H), 3129 (N–H). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.28 (t, $^3J(^1H\text{-}^1H)$ = 7 Hz, 9H, triethylammonium CH_3), 1.78 (s, 3H, Ar–CH_3^{16}), 1.94 (s, 6H, Ar–$CH_3^{7,25}$), 2.09 (s, 9H, Ar–$CH_3^{8,17,26}$), 3.12 (q, $^3J(^1H\text{-}^1H)$ = 7 Hz, 6H, triethylammonium NCH_2), 3.33 (d, $^2J(^1H\text{-}^1H)$ = 13 Hz, 3H, $NCH_2^{9,27}$), 3.71 (br., 2H, NCH_2^{18}), 4.81 (d, $^2J(^1H\text{-}^1H)$ = 13 Hz, 3H, $NCH_2^{9',27'}$), 5.65 (s, 1H, H^{14}), 6.40 (s, 1H, H^{12}), 6.50 (s, 3H, $H^{5,23}$), 6.63 (s, 3H, $H^{3,21}$), 8.78 (br., 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 8.86 (triethylammonium CH_3), 16.09, 16.14, 16.44 (Ar–$CH_3^{7,16,25}$), 20.13, 20.31, 20.33 (Ar–$CH_3^{8,17,26}$), 47.03 (triethylammonium NCH_2), 58.47, 63.26 ($NCH_2^{9,18,27}$), 120.21, 122.23 ($C^{6,15,24}$), 125.21, 126.72 ($C^{2,11,20}$), 127.81, 128.20 ($C^{5,14,23}$), 129.43, 129.75 ($C^{3,12,21}$), 131.89, 133.91 ($C^{4,13,22}$), 151.14, 157.74 ($C^{1,10,19}$), 172.44 (NCS). ^{119}Sn (149 MHz, $CDCl_3$): δ (ppm) -704. MS: m/z (relative abundance (%) assignment): 652 (100) $[M - (C_2H_5)_3NH]^+$, 625 (14.72) $[M - (C_2H_5)_3NH - 2CH_3 + 2H]^+$, 609 (10.14) $[M - (C_2H_5)_3NH - 3CH_3 + H]^+$, 179 (174.41) $[OPh(CH_3)_2CH_2N{+}NH_3]^+$. $C_{35}H_{46}N_4O_3S_2Sn$ (753.60): calcd. C 55.78, H 6.15, N 7.43, S 8.51; found C 55.77, H 5.89, N 6.88, S 8.34.

*2.3.4. Optical studies of **2***

Stock solution of compound **2** (5 mM) and metal salts (10 mM) were prepared by dissolving requisite amounts in methanol and acetone. To study the colorimetric response of **2**, 2 mL of its stock solution was mixed with 2 mL of respective metal ion solution (Mn^{2+}, Cd^{2+}, Cr^{3+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}; 0.5 mM each). The change in colour of the solution was recorded immediately. The same solution was used to record the UV-vis spectrum.

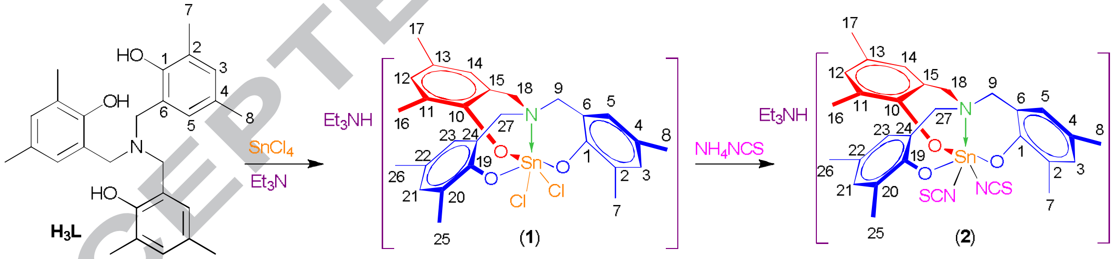
In order to complete the titration and record the response of **2** towards increasing concentration of Fe^{3+}, Cu^{2+} and Co^{2+}, 2 mL solution of **2** (0.2 mM) was filled in a quartz optical cell of 1 cm optical path length, and 0.04 mL of the solution of metal ions (0.2 mM) were added gradually by using a micropipette. After 2 min of the mixing of metal ions with **2**, UV-vis absorption spectra were measured at room temperature.

For Job plot analyses, 0.2 mM solution of metal ions (Fe^{3+}, Cu^{2+} and Co^{2+}) and 0.2 mM of **2** was prepared, and a titration was performed under the condition that mole fraction of metal ions gradually increases from 0 to 1 in final solution (5 mL).

To compare the chelating behaviour of **2**, NH_4SCN and **H_3L**, different test solutions were prepared by mixing their equimolar solutions (1 mM) with the metal ions (Fe^{3+}, Cu^{2+} and Co^{2+}; 1 mM each) in different ratios (for details see **table S1**).

3. Results and discussion

In the present work, a C_3 symmetric aminotrisphenolate ligand was used to obtain monomeric fused [4.4.4.0^{1,6}] heterotricyclic tin compounds. The tricyclic cage of **H_3L** was substituted with bulky phenyl groups, which provided non-flexibility to the arms. Moreover, the rigidity of tripodal arms transformed the oligomerizable active centres of ligating system into inactive sites. Owing to the stability offered by trisphenolate ligating system and formation of monomeric fused heterotricyclic cages in the past, we tried to yield a chloro derivative of fused [4.4.4.0^{1,6}] heterotricycle (i.e LSnCl) to use as a precursor for obtaining its rhodanide derivative (i.e. LSnNCS). Unexpectedly, the reaction yielded compounds **1** and **2** as triethylammonium salts (**Scheme 1**). The most interesting feature of these compounds is incorporation of an extra exocyclic substituent leading to hexcoordination at Sn centre. The formation of **1** and **2** was confirmed by IR and NMR (^{1}H, ^{13}C, ^{119}Sn) spectroscopy, mass spectrometry, elemental analysis and single-crystal X-ray diffraction studies (only for **2**).



Scheme 1. Synthetic routes to compound **1** and **2** (isolated and expected products).

The solid state FT-IR spectrum of ligand **H_3L** features vibration bands at 3517 and 3362 cm^{-1} due to free and hydrogen bonded –OH groups, which disappeared in the IR spectra of **1** and **2**, thereby confirming its role as L^{3-} ligating system. Apart from this, **1** and **2** showed the corresponding Sn–O and Sn–N bands in their respective regions, i.e., 537 and 538 cm^{-1} for Sn–O, 417 and 418 cm^{-1} for Sn–N, respectively. The mass spectrum of **1** consisted of peaks at m/z 606 (**1** lacking triethylammonium ion) and 536 (**1** lacking triethylammonium and both chloride substituents) suggesting the presence of the heterotricycle. In the mass spectrum of

2, a sharp peak corresponding to the heterotricyclic cage with two –NCS substituents appeared as a base peak at m/z 652.

^{1}H NMR spectrum of **1** (crude) showed relatively broad signals in the respective regions for some of the protons either due to the ring inversion of skeleton or flipping between endo and exo form [38,39], however, corresponding signals for **2** were relatively clear. The ^{1}H NMR spectrum of compound **1** and **2** supported the formation of the stannatrane-like cage. ^{1}H NMR data revealed that the anion has mirror symmetry, and in compound **2** the SCN ligands, Sn atom, N1 and the aryl which belongs to O2 are constituents of the mirror plane. Hence, the N-CH_2 protons of this group are chemically equivalent and produce a singlet at 3.73 and 3.71 ppm for **1** and **2**, respectively. The other two aryls (at O1 and O3) are chemically equivalent, but they have two different protons of their NCH_2 groups, one of them points towards the NCS ligand and the other one points towards the aryl which is in the mirror plane. The presence of two doublets for NCH_2, δ = 3.16/5.25 ppm ($^{2}J(^{1}H-^{1}H)$ = 11 Hz) for **1** and 3.33/4.81 ppm ($^{2}J(^{1}H-^{1}H)$ = 13 Hz), for **2** suggested different environment for the protons, and are, therefore diastereotopic. This is also supported by the presence of four signals at 5.60, 6.37, 6.47, 6.59; and 5.65, 6.40, 6.50, 6.63 for aromatic protons as well as splitting of signals of aryl-methyl groups in ratio 3:6:9 and 3:6:6:3, respectively for **1** and **2**. ^{119}Sn spectra in $CDCl_3$ showed signals at -624 for **1** and -709 ppm for **2** corroborating hexacoordination at Sn. The ^{119}Sn NMR signal for **2** showed splitting due to ^{119}Sn–^{15}N coupling [40,41] (**Fig. S1**).

3.1. Crystal Structure

Single-crystal X-ray diffraction analysis of **2** revealed formation of an ionic compound with fused [4.4.4.0^{1,6}] heterocyclic anion (featuring hexacoordinated Sn) and triethylammonium as cation (**Fig. 1**). The compound was isolated as monomer with distorted octahedral geometry of Sn, in which NCS substituents are cis to each other. The tetradentate L^{3-} is coordinated in such a way that its N atom and one of the oxygen atoms are situated *trans* to the –NCS groups. Because of steric constraints, this ligating system indeed disfavoured the formation of oligomers even in the case of tin where oligomerisation or formation of clusters is very common. Nonetheless, it still supported the formation of an octahedral tin coordination sphere with the aid of a small monodentate ligand.

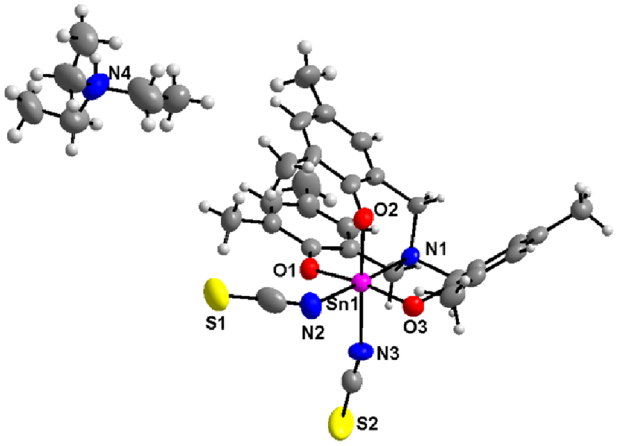


Fig. 1. ORTEP presentation (thermal ellipsoids at 40 % probability whereas hydrogens at 10 % probability) of **2** with partial numbering scheme.

In spite of the different trans-donor situations, the three Sn–O bond lengths are essentially the same (Sn–O1 2.022(3), Sn–O2 2.021(3) and Sn–O3 2.016(3) Å). The Sn–N(thiocyanate) bond lengths are more responsive to their different trans-donor situations: Sn–N2 2.155(5) and Sn–N3 2.178(4) Å. Both thiocyanate units are nearly linear (N2–C28–S1 176.2(6)°, N3–C29–S2 177.4(5)°) and the Sn–N–C–S tetratomic chains are bent at the nitrogen atoms (Sn1–N2–C28 128.8(5)°, Sn1–N3–C29 159.6(5)°). The difference in the Sn–N–C bond angles is accompanied with significant differences in N–C bond lengths in the two –NCS groups (N2–C28 1.162(8), N3–C29 1.121(7) Å).

Generally, fused heterocycles form propeller like structure with symmetrical orientation of tripodal arms. However, in the present molecule, propeller-like arrangement is lost due to the second thiocyanate group, thus furnishing an octahedral coordination sphere about tin. Interestingly, the transannular Sn–N bond (2.244(4) Å, **Table 1**) observed in this molecule belongs to the shortest observed in that kind of tin compounds, together with short transannular Sn–N bonds in some stannatranes with fused five-membered rings, i.e., $N(CH_2CMe_2O)_3SnOC_6H_4NO_2$ (2.232(2) Å) and $N[CH_2C(O)O]_3Sn(CH_2)_3N(O)Me_2$ (2.231(7) Å)^{19}, while various other stannatranes exhibit longer transannular Sn–N bonds (e.g., compounds of the type $N(CH_2CMe_2O)_3SnX$ (X = OR, SR, halogen) (2.248(2)-2.295(3) Å) [13], $[N(CH_2CH_2O)_3SnMe]_3$ (2.28 Å) [16], $[N(CH_2CH_2O)_3SnR]$ (R = *t*-Bu, 2.324 Å [18]; R = C_6H_4-*o*-OMe, 2.323(7) Å [17]), $N(CH_2CH_2O)_3SnOs(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ (2.422(4) Å) [42] and psuedostannatranes with aminobisphenolate moiety of type $[N\{CH_2(C_6H_2Me_2)O)\}_3SnBu]_2$ (2.256(2) Å) and $[\{CH_2(C_6H_2Me_2)O)\}_3SnPh\cdot OSnPh_2]_2$ (2.264(2) Å) [15]). This may be attributed to the electron withdrawing effect of –NCS substituents, which is also corroborated by the shortening of transannular Si–N bond observed in 1-isothiocyanatosilatrane [43].

Table 1. X-ray crystal data of selected bond lengths (Å) and angles (°).

Bond lengths (Å)		Bond Angles (°)	
Sn(1)-O(av)	2.019(3)	O(1)-Sn(1)-O(2)	95.7(3)
Sn(1)-N(1)	2.244(4)	O(1)-Sn(1)-O(3)	170.3(3)
Sn(1)-N(2)	2.155(5)	O(2)-Sn(1)-O(3)	93.93(14)
Sn(1)-N(3)	2.178(4)	O(1)-Sn(1)-N(2)	89.01(17)
S(1)-C(28)	1.611(8)	O(2)-Sn(1)-N(2)	92.93(17)
S(2)-C(29)	1.612(6)	O(3)-Sn(1)-N(2)	91.51(17)
N(2)-C(28)	1.162(8)	O(1)-Sn(1)-N(3)	86.10(16)
N(3)-C(29)	1.121(7)	O(2)-Sn(1)-N(3)	178.12(17)
N(1)-C(9)	1.501(6)	O(3)-Sn(1)-N(3)	84.28(17)
N(1)-C(18)	1.506(6)	O(1)-Sn(1)-N(1)	87.90(14)
N(1)-C(27)	1.511(6)	O(2)-Sn(1)-N(1)	86.87(13)
O(1)-C(1)	1.343(6)	O(3)-Sn(1)-N(1)	91.62(14)
O(2)-C(10)	1.357(6)	N(2)-Sn(1)-N(3)	87.69(19)
O(3)-C(19)	1.355(6)	N(2)-Sn(1)-N(1)	176.86(18)
		N(3)-Sn(1)-N(1)	92.61(16)

In the crystal structure, the triethylammonium cation is two-fold disordered with nearly equal occupancy of the two conformations. In spite of this disorder, the N-H groups are in similar orientation and there are weak interactions between the cation Et_3NH^+ and anion $[LSn(NCS)_2]^-$. Specifically, the closest contact between cation and $[LSn(NCS)_2]^-$ involves a nitrogen atom of thiocyanate and a H atom of the Et_3NH^+ cation (N2–H4/N2–H4A = 2.424/2.094 Å) and are within the sum of van der Waals radii for nitrogen and hydrogen (2.75 Å), consistent with weak cation-anion interactions [44]. This interaction can be interpreted as a contributor to the different Sn-N-C angles encountered with the two NCS ligands in this tin complex.

The packing of compound consisted of compact arrangement of fused heterotricyclic anion and triethylammonium cation in a zig-zag fashion owing to the persisting Van der Waal forces (**Fig. S2**). These arrangements can be viewed in plane as a group of butterflies moving in same direction. Selected parameters of data collection and structure refinement are given in **Table S2**.

3.2.Chromogenic and optical response of ***2***

A very interesting feature of **2** is its capability to act as a chromoreactand (chromogenic reactand) towards some metallic species such as Fe^{3+}, Cu^{2+} and Co^{2+} ions. A solution of **2** switched its colour immediately to light orange (Fe^{3+}), peach (Cu^{2+}) and blue (Co^{2+}) in acetone, and pink (Fe^{3+}), and green (Cu^{2+}) in methanol even in the presence of low concentrations of these metal ions (0.005, 0.115 and 0.214 mM for Fe^{3+}, Cu^{2+} and Co^{2+}, respectively). This particular characteristic of **2** was attributed to the presence of rhodanide antennae, which have high tendency to coordinate metal ions via S, thereby inducing a rapid colour change. In contrast, other metal ions (0.5 mM) including Mn^{2+}, Cd^{2+}, Cr^{3+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+} did not induce any colour change in **2** (5 mM) (**Fig 2**).

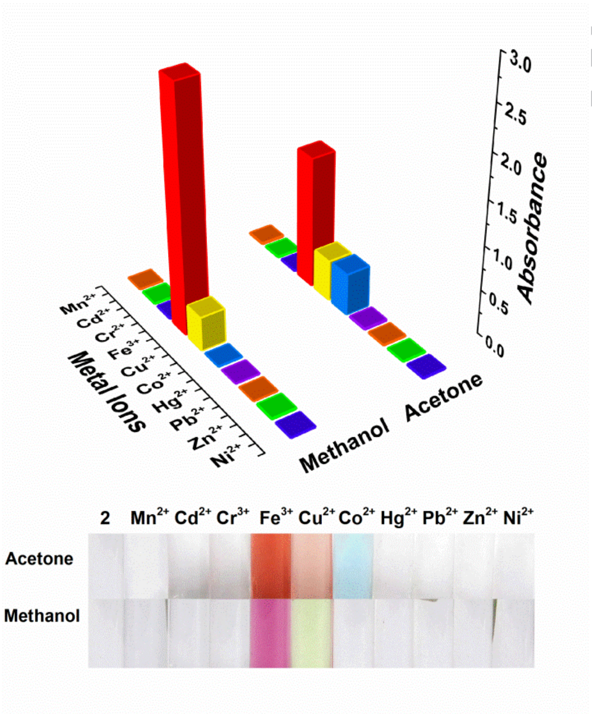


Fig. 2. Top: Column chart illustrating the optical response of **2** (5 mM) against different metal ions (0.5 mM) in methanol (λ_{max} = 519 and 391 nm for Fe^{3+} and Cu^{2+} ions, respectively) and acetone (λ_{max} = 467, 472 and 623 nm for Fe^{3+}, Cu^{2+} and Co^{2+}, respectively); Bottom: Chromogenic response of **2** towards different metal ions in methanol and acetone (Left to right: **2**, Mn^{2+}, Cd^{2+}, Cr^{3+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}).

The UV-Vis spectrum of pure $\mathbf{H_3L}$ showed an intense band at 286 nm, which was also observed in case of **2**. The colourless solution of **2** (0.2 mM) in methanol showed a split peak with maxima at 235 and 287 nm with no absorption band in the visible region. After addition of metal ions to the solution of **2**, the consistency of these bands in addition to an extra band in the visible region suggested the retention of the tricyclic framework of the receptor even after the addition of metal ions and involvement of thiocyanate antennae in the chromogenic switch.

The switching of colour may be ascribed to the coordination of metal with **2** via S atoms, which is also supported by the origin of extra band in the absorption spectrum of methanolic solution of **2** on the addition of Fe^{3+} and Cu^{2+} ions. The band centred at 519 (19269 cm^{-1}) in the presence of Fe^{3+} ions can be assigned to LMCT transition (i.e from oxidizable thiocyanate to oxidizing Fe^{3+}) and the absorption band centred at 391 nm (25575 cm^{-1}) in the presence of Cu^{2+} ions may be attributed to the LMCT from π NCS to Cu^{2+} orbitals [45]. Solvatocromism studies of the metal complexes showed some interesting changes in the chromogenic and optical properties of compound **2** in the presence of metal ions. The change in solvent from methanol to acetone showed both the hypochromic and hypsochromic shift in the absorption bands of **2** and also 'turned on' a colorimetric and optical switch for Co^{2+} ions (which was absent in methanol) (**Fig. S3**). The UV-Vis spectrum of Co^{2+} ions in acetone exhibited absorption band at 623 nm (16050 cm^{-1}) with a shoulder at 589 nm (16978 cm^{-1}), which clearly indicated tetrahedral geometry acquired by rhodanides around Co^{2+} ions. The origin of bands can be ascribed to d-d transitions from ground state $^4A_2$ to higher energy levels, which is also supported by literature [46]. The absorption maxima for Fe^{3+} and Cu^{2+} in acetone were observed at 467 (21413 cm^{-1}) and 472 nm (21186 cm^{-1}), respectively (**Fig. 2**). The chromogenic and optical change in **2** at different concentration of metal ions (**Fig. 3**) showed a continuous rise in the intensity of colour and corresponding absorption maxima with increasing concentration of metal ions in methanol (except for Co^{2+} which was taken in acetone). It is clear that methanolic solution of **2** did not absorb in the visible region, however, on adding metal ions it showed a drastic increase in absorption centered at 519, 391 and 623 nm (Fe^{3+}, Cu^{2+} and Co^{2+} respectively). On the basis of Job's plot 1:2 colored complexes $[M\{(NCS)_2SnL\}_2]$ [47-49] can be expected for M = Co^{2+}, Cu^{2+} and Fe^{3+} ions (**Fig. 4**).

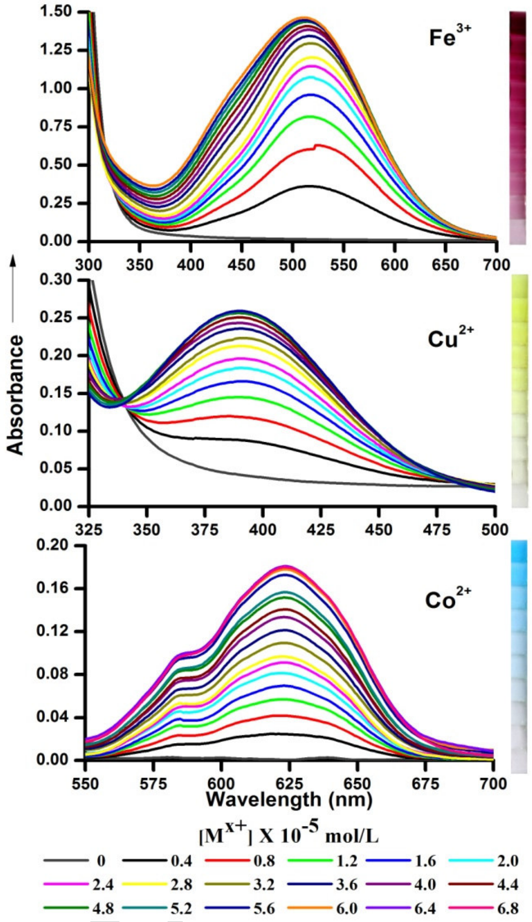


Fig. 3. UV-vis absorption spectra of **2** (0.2 mM) with different concentration of Fe^{3+}, Cu^{2+} in methanol and Co^{2+} in acetone and the corresponding colour change of the sensor **2** on increment of metal ion concentration.

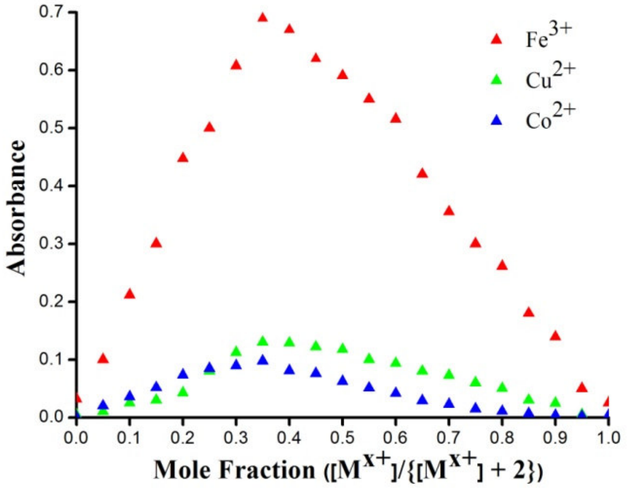


Fig. 4. Job plot for complexation of sensor **2** (0.2 mM) with Fe^{3+}, Cu^{2+} and Co^{2+} (0.2 mM).

Moreover, similar type of studies were accomplished using **H_3L** and ammonium thiocyanate solutions under similar conditions to confirm the participation of –NCS moieties in the chromogenic response of **2** (**Fig. S4, S5, S6**). The studies failed to show significant chromogenic response of **H_3L** on the addition of metal ions. In contrast, similar type of absorption bands were observed in case of ammonium thiocyanate but their intensity was low as compared to **2**. A table summarizing the wavelengths, concentration and molar absorptivity is given below to compare the optical properties of **2**, **H_3L** and ammonium thiocyanate under similar conditions (**Table 2**). The studies revealed **2** as a better chromoreactand because it can bind metal ions more effectively as compared to free –NCS (in ammonium thiocyanate). The effective chelation in **2** may be attributed to the presence of –NCS in cis positions. The regression plots revealed the linearity of optical response up to 0.0761, 0.0761 and 0.0615 for Fe^{3+}, Cu^{2+} and Co^{2+}, respectively (**Fig 5**). The limit of detection for colorimetric response was found to be 0.005, 0.115 and 0.214 mM for Fe^{3+}, Cu^{2+} and Co^{2+}, respectively. Hence, **2** may be used as an alternative for the naked eye and optical recognition of these metal ions.

Table 2. Comparison of optical response of equimolar solutions (1mM each) of **2** (1 equiv), NH_4SCN (2 equiv) and **H_3L** (1 equiv) towards metal ions (1 mM); see Table S1 for more details.

Metal ions	Chromogenic Reactand	Wavelength (nm), Wavenumber (cm^{-1})	Absorbance	Molar Absorptivity, ε x 10^5 (m^2/mol)
Fe^{3+}	**2**	527 (18975)	0.504	5.038 (LMCT)
	NH_4SCN	521 (19194)	0.232	1.161 (LMCT)
	H_3L	371 (26954)	0.320	3.204
Cu^{2+}	**2**	390 (25641)	0.075	0.755 (LMCT)
	NH_4SCN	383 (26110)	0.059	0.295 (LMCT)
	H_3L	466 (21459)	0.043	0.435
Co^{2+}	**2**	623 (16051)	0.058	0.579 (d-d)
	NH_4SCN	623 (16051)	0.074	0.371 (d-d)
	H_3L	510 (19608)	0.014	0.138

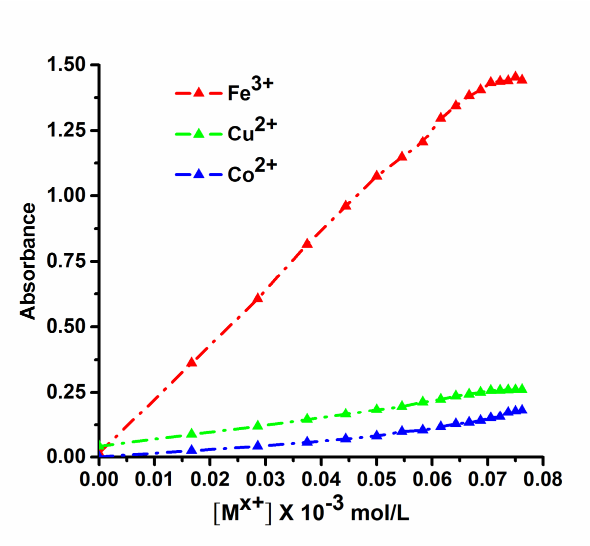


Fig. 5. Regression plot for the variation of optical response of **2** (0.2 mM) towards Fe^{3+}, Cu^{2+} and Co^{2+} ions at 519 nm, 391 nm and 623 nm, respectively.

4. Conclusions

Fused [4.4.4.0^{1,6}] heterotricyclic metallorganic compounds of Sn were successfully achieved as triethylammonium salts. The compounds were isolated as monomers in which Sn was hexacoordinated. The hexacoordination in compounds was achieved by incorporation of an extra exocyclic substituent. The presence of –NCS antennae in **2** made it sensitive towards metal ions Co^{2+}, Cu^{2+} and Fe^{3+}, which switched its color immediately on the addition of metal ions. Therefore, **2** may be used for the recognition of some metal ions, which induce different colours and show solvatochromism behaviour.

Acknowledgements

Authors are thankful to UGC, New Delhi [17-06/2012 (i) EU-V], DST, New Delhi [Regd No. CS-099/2012] and PURSE-II for providing financial support.

Appendix A. Supplementary data

CCDC 968635 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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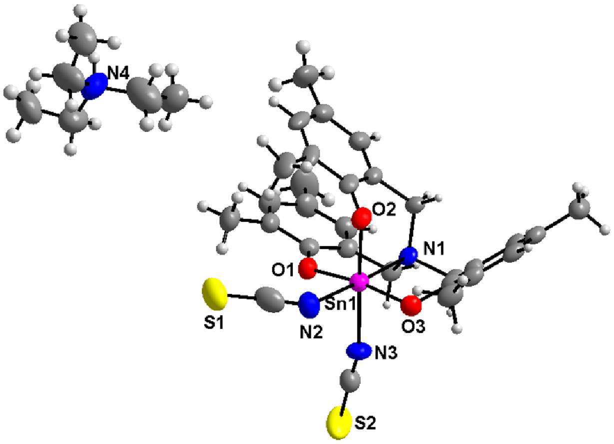
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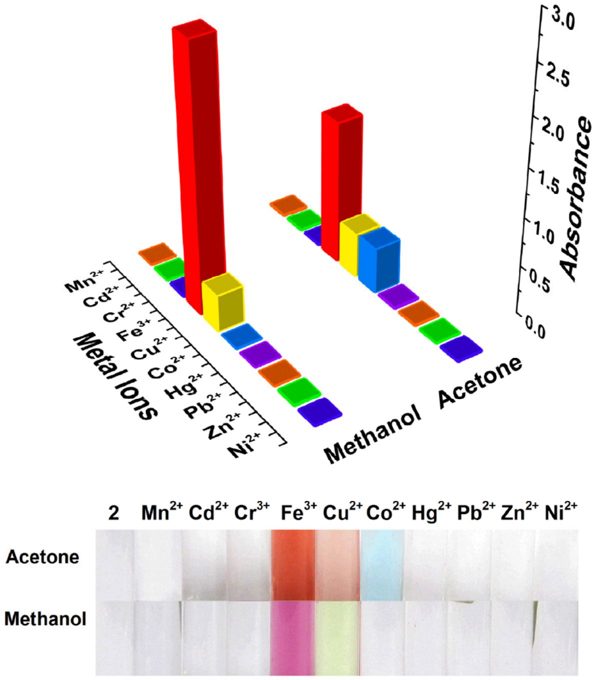
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Pb2+
Zn2+
Ni2+
Methanol
Acetone
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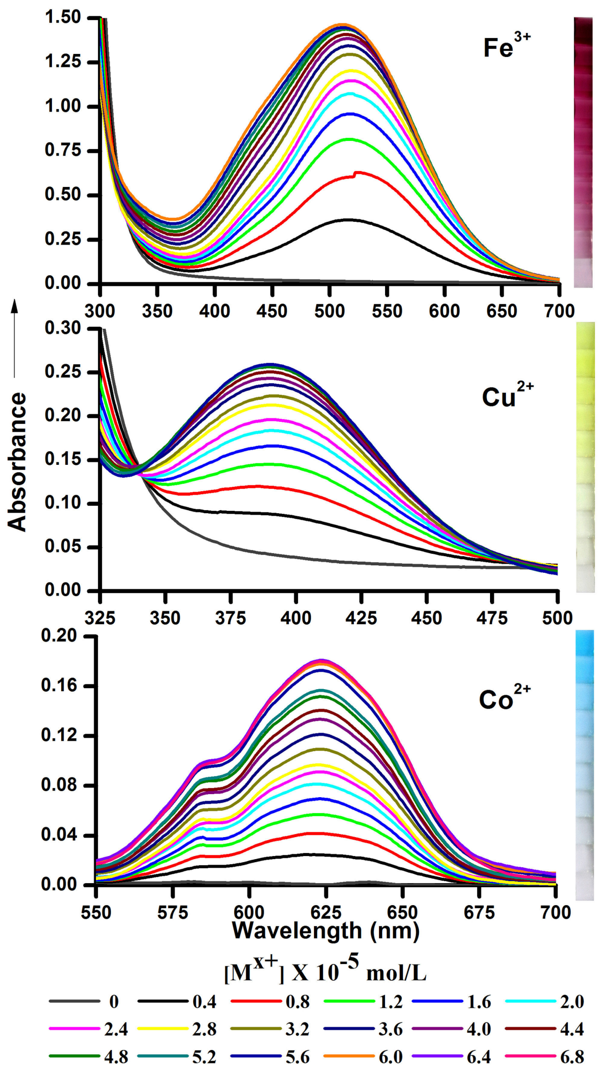
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375
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475
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Absorbance
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575
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675
700
Wavelength (nm)
[M^{X+}] X 10^{-5} mol/L
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2.0
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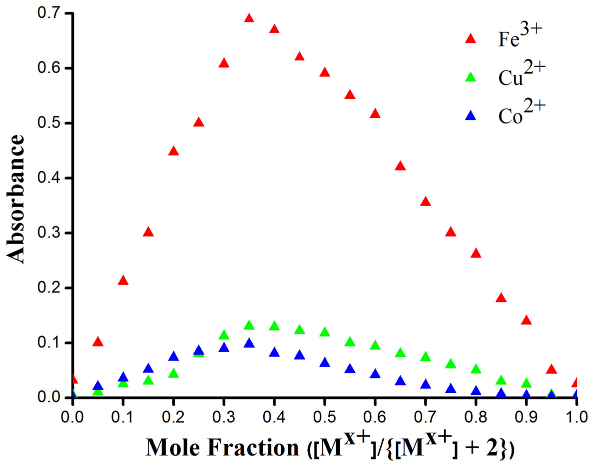

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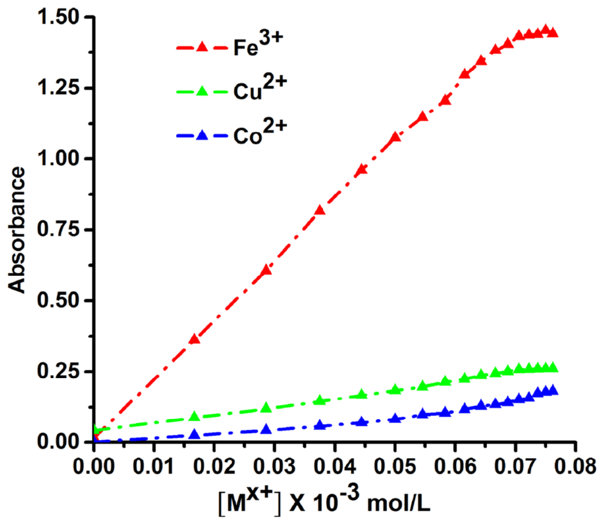
0.7
0.8
0.9
1.0
Mole Fraction ([M^{x+}]/{[M^{x+}] + 2})
▲ Fe^{3+}
▲ Cu^{2+}
▲ Co^{2+}


Fe^{3+}
Cu^{2+}
Co^{2+}
Absorbance
1.50
1.25
1.00
0.75
0.50
0.25
0.00
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
[M^{x+}] X 10^{-3} mol/L

Highlights

- Synthesis of noval fused [4.4.4.0^{1,6}] heterotricyclic metallorganic compounds of Sn as triethylammonium salts using phenolic ligand [Tris(2-hydroxy-4,6-dimethylbenzyl)amine] **H_3L**.
- Rhodanide tailored hexacoordinated psuedostannatrane (**2**) with –NCS antennae act as one of the rare examples of chromophoric probes
- Rapid, sensitive and selective colorimetric sensing of Fe^{3+}, Cu^{2+} and Co^{2+} ions