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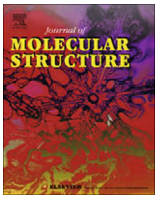

Syntheses, structures and properties of homo- and heterobimetallic complexes of the type $[Zn(tren)NCS]_2[M(NCS)_4]$ [tren = tris(2-aminoethyl)amine; M = Zn, Cu]

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ABSTRACT

A 2:2:1:6 molar ratio of $Zn(ClO_4)_2·6H_2O$, tris(2-aminoethyl)amine (tren), $Zn(ClO_4)_2·6H_2O/Cu(ClO_4)_2·6H_2O$ and NH_4NCS in methanol–water solution mixtures affords homo-/heterobimetallic compounds of the type $[Zn(tren)NCS]_2[M(NCS)_4]$ (M = Zn, **1**; M = Cu, **2**) which have been characterized using microanalytical, spectroscopic, magnetic and other physicochemical results. The structures of the compounds are determined by X-ray diffraction measurements. Structural analyses reveal that **1** and **2** are isomorphous and consist of two discrete $[Zn(tren)NCS]^+$ cations and a $[M(NCS)_4]^{2-}$ (M = Zn/Cu) anion. Zinc(II) centers in the $[Zn(tren)NCS]^+$ units adopt distorted trigonal bipyramidal geometry with ZnN_5 chromophores coordinated through four N atoms of tren and one N atom of terminal thiocyanate. Each metal(II) center in $[M(NCS)_4]^{2-}$ has a distorted tetrahedral coordination environment with an MN_4 chromophore ligated by four N atoms of the terminal thiocyanates. In solid state, doubly N–H…S hydrogen bonded 1D chains of $[Zn(tren)NCS]^+$ cations are interconnected by tetrahedral $[Zn(NCS)_4]^{2-}/[Cu(NCS)_4]^{2-}$ anions through cooperative N–H…S and N–H…N (in **1**) and N–H…S and C–H…S (in **2**) hydrogen bonds resulting in 3D network structures. Establishment of such networks seems to be aiding the crystallization.

1. Introduction

The importance of hydrogen bonds [1–3] in the context of supramolecular chemistry [4–6], crystal engineering [7,8] and molecular recognition [9,10] has been well recognized in recent times. This secondary interaction has ramifications in systematic design of new functional materials [11–14]. Bifunctional ligands that contain both metal ion binding groups and hydrogen bond donor and acceptor centers have pivot influence in the rational design of different metal–organic frameworks (MOF's) with tunable properties. Pseudohalides like azide and thiocyanate are well known [15–17] for their versatile coordination motifs resulting in different 1D, 2D and 3D coordination polymers and polymer-based superstructures. Self-assembly [18] of the metal ions as geometry setters, organic ligands as spacers and pseudohalides as covalent and/or non-covalent bridges is an efficient approach to construct different metal–organic coordination frameworks [19,20]. A popular approach in coordination chemistry is the use of cyanometallates $[M(CN)_n]^{Z-}$ ($M = V^{II}$, Cr^{III}, Mn^{III} and Fe^{III}, $n = 6$, $Z = 4$ or 3; $M = Ni^{II}$, $n = 4$, $Z = 2$; $M = Mo^V$, $n = 8$, $Z = 3$) with multiple connectors to prepare multidimensional polymers and polymer-based superstructures in combination with suitable complementary units containing potential acceptor sites [21–23]. Recently, we are interested to extend this view with other hexapseudohalogenometallates specially with thiocyanate and reported the use of molecular ions $[Cd(NCS)_6]^{4-}$ and $[Mn(NCS)_6]^{4-}$ as multiple connectors [24–26] with suitable complementary units containing 3d/4d metal–ion centers ligated by tris(2-aminoethyl)amine (tren) and with potential acceptor sites. A range of molecular and crystalline architectures with different homo- and heteropolymers and bimetallic complexes is the result from such study. $[Cd(NCS)_6]^{4-}$ forms 2D polymers of the type $[Cd_3(tren)_2(NCS)_6]_n$, $[Ni_2Cd(tren)_2(NCS)_6]_n$ [24] and a trinuclear compound $[Cu_2Cd(tren)_2(NCS)_6]$ [25]; but $[Mn(NCS)_6]^{4-}$ in combination with $[Cu(tren)(NCS)]^+$ results in a bimetallic complex of the type $[Cu(tren)(NCS)]_4[Mn(NCS)_6]$ [26] with hydrogen bonded network instead of covalently bonded polymers showing hydrogen bonding as the key factor in this complex leading to superstructure. Keeping in mind such difference in behaviour of cadmium(II) and manganese(II), we have extended this work with tetrapseudohalogenometallate such as $[M^{II}(NCS)_4]^{2-}$ (M = Zn and Cu). The two 3d ions copper(II) and

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zinc(II) find significant use in bioinorganic chemistry [27–30]. A 2:2:1:6 molar ratio of $Zn(ClO_4)_2{\cdot}6H_2O$, tren, $Zn(ClO_4)_2{\cdot}6H_2O$/$Cu(ClO_4)_2{\cdot}6H_2O$ and NH_4NCS in aqueous methanol gives rise to bimetallic compounds of the type $[Zn(tren)NCS]_2[M(NCS)_4]$ (M = Zn, **1**; M = Cu, **2**). Single crystal X-ray crystallographic studies show the presence of discrete $[Zn(tren)NCS]^+$ and $[Zn(NCS)_4]^{2-}$ in **1** and, $[Zn(tren)NCS]^+$ and $[Cu(NCS)_4]^{2-}$ in **2** which are hydrogen bonded to form 3D continuum. The details of syntheses, structures and other physicochemical properties are described below.

2. Experimental

2.1. General remarks and physical measurements

2.1.1. Materials

High purity tris(2-aminoethyl)amine (Fluka, Germany), ammonium thiocyanate (E. Merck, India), copper(II) carbonate (E. Merck, India), zinc(II) carbonate (E. Merck, India) and perchloric acid (E. Merck, India) were purchased from respective concerns and used as received. Copper(II) and zinc(II) perchlorate hexahydrates were prepared [31] by treatment of their respective carbonates with perchloric acid followed by slow evaporation on a steam-bath, filtration through a fine glass-frit, and preserved in a desiccator containing concentrated sulfuric acid (E. Merck, India) for subsequent uses. All other chemicals and solvents were AR grade and used as received. The synthetic reactions and work-up were done in open air.

Caution! Perchlorate compounds of metal ions are potentially explosive [32] especially in the presence of organic ligands. Only a small amount of these materials should be prepared and handled with care.

2.1.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were obtained using a Perkin-Elmer 2400 CHNS/O elemental analyzer. IR spectra (KBr discs, 4000–300 cm^{-1}) were recorded using a Perkin-Elmer FTIR model RX1 spectrometer. Molar conductances were measured using a Systronics conductivity meter where the cell constant was calibrated with 0.01 M KCl solution, and dry MeCN was used as solvent. Room temperature magnetic susceptibility measurement was made on a CAHN electrobalance 7550 with $Hg[Co(SCN)_4]$ as reference and diamagnetic corrections were done using Pascal's constants [33]. UV–vis (in MeCN) and reflectance spectra (in Nujol) were recorded with a Jasco model V-570 UV–vis–NIR spectrophotometer.

2.2. General syntheses of $[Zn(tren)NCS]_2[Zn(NCS)_4]$ (**1**) and $[Zn(tren)NCS]_2[Cu(NCS)_4]$ (**2**)

The homo- and heterobimetallic complexes **1** and **2** were prepared by the reaction of $Zn(ClO_4)_2{\cdot}6H_2O$, tren, NH_4NCS and $Cu(ClO_4)_2{\cdot}6H_2O$ (applicable for **2**) in aqueous methanol at room temperature using three different procedures with varied yields. These are described below.

2.2.1. Method A

A methanolic solution (10 mL) of $Zn(ClO_4)_2{\cdot}6H_2O$ (0.372 g, 1 mmol) was added dropwise to a solution of NH_4NCS (0.304 g, 4 mmol) in the same solvent (5 mL) resulting in a colourless solution. In an another container $Zn(ClO_4)_2{\cdot}6H_2O$ (0.372 g, 1 mmol) and tren (0.146 g, 1 mmol) were mixed together in water (15 mL) producing a colourless solution. The former was added dropwise to the latter that results in a clear colourless solution. This was filtered and kept in open air for evaporation. After a few days colourless crystals of **1** suitable for X-ray diffraction were obtained that were collected by filtration, washed with hexane and dried *in vacuo* over silica gel indicator; the yield was 0.402 g (48%). Compound **2** was prepared [yield: 0.434 g (52%)] similarly except that $Cu(ClO_4)_2{\cdot}6H_2O$ (0.370 g, 1 mmol) in place of $Zn(ClO_4)_2{\cdot}6H_2O$ was added to the solution of NH_4NCS.

2.2.2. Method B

Tren (0.293 g, 2 mmol) in water (5 mL) and NH_4NCS (0.152 g, 2 mmol) in the same solvent (5 mL) were added slowly to an aqueous solution (5 mL) of $Zn(ClO_4)_2{\cdot}6H_2O$ (0.745 g, 2 mmol) in a beaker. In an another container NH_4NCS (0.304 g, 4 mmol) and $Zn(ClO_4)_2{\cdot}6H_2O$ (0.372 g, 1 mmol) were mixed slowly in methanol (15 mL). These two solutions were mixed together resulting in a colourless mixture. This was filtered and kept in open air for evaporation. Colourless crystals of **1** were formed after 2 weeks. The yield was 0.712 g (85%). **2** was prepared [yield: 0.668 g (80%)] using the same procedure except that $Cu(ClO_4)_2{\cdot}6H_2O$ (0.370 g, 1 mmol) in place of $Zn(ClO_4)_2{\cdot}6H_2O$ was added to NH_4NCS (0.304 g, 4 mmol).

2.2.3. Method C

$Zn(ClO_4)_2{\cdot}6H_2O$ (1.117 g, 3 mmol), tren (0.293 g, 2 mmol) and NH_4NCS (0.457 g, 6 mmol) were mixed in a single container containing 30 mL of methanol–water (1:1) producing a clear colourless solution. This was filtered and kept in open air for evaporation. Colourless crystals of **1** were formed after 1 week; the yield was 0.293 g (35%). Compound **2** was isolated [yield: 0.351 g (42%)] by the mixing of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.370 g, 1 mmol), $Zn(ClO_4)_2{\cdot}6H_2O$ (0.745 g, 2 mmol), tren (0.293 g, 2 mmol) and NH_4NCS (0.457 g, 6 mmol) in a single container following the same procedure as above.

The analytical, solution electrical conductivity, spectroscopic and magnetic results obtained for the compounds **1** and **2** from Methods A to C are akin which are listed here. *Anal.* Calc. for $C_{18}H_{36}N_{14}S_6Zn_3$ (**1**): C, 25.8; H, 4.3; N, 23.5. Found: C, 25.6; H, 4.1; N, 23.2%. Λ_M (MeCN, $ohm^{-1}\,cm^2\,mol^{-1}$): 110. IR (KBr, cm^{-1}): ν(N–H) 3292, 3241; ν(C–H) 2969, 2920; ν(NCS) 2096, 2088; ν(C–S) 743. UV–vis (λ, nm): 271. *Anal.* Calc. for $C_{18}H_{36}N_{14}S_6CuZn_2$ (**2**): C, 25.8; H, 4.3; N, 23.6. Found: C, 25.5; H, 4.1; N, 23.2%. Λ_M (MeCN, $ohm^{-1}\,cm^2\,mol^{-1}$): 115. IR (KBr, cm^{-1}): ν(N–H) 3296, 3244; ν(C–H) 2964, 2918; ν(NCS) 2092, 2082; ν(C–S) 740. UV–vis (λ, nm): 833, 362, 266. μ_{eff}: 1.79 BM.

2.3. X-ray crystallography

Single crystals of **1** and **2** suitable for X-ray analyses were selected from those obtained by open evaporation of methanol–water solution mixtures (1:1) at 298 K. Crystallographic data were collected on a Bruker SMART APEXII CCD area-detector diffractometer with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K with the Oxford Cryosystem Cobra low-temperature attachment. The collected data were reduced using SAINT and the empirical absorption corrections were performed using SADABS program [34]. A summary of the crystallographic data and structure determination parameters is given in Table 1. Of 23,400 and 19,771 collected reflections, 9761 and 9510 unique reflections were recorded in **1** and **2**, respectively. The structures were solved by direct methods using SHELXTL [35]. All hydrogen atoms were placed in calculated positions, with N–H = 0.90 Å and C–H = 0.97 Å and refined isotropically and the U_{iso} values were constrained to be $1.2U_{eq}$ of the carrier atoms. For compound **1**, the two CH_2CH_2 groups are disordered over two orientations with the occupancies of 0.71037(01) and 0.28963(01) for C1BA, C2BA, C3BA, C4BA and C1BB, C2BB, C3BB, C4BB, respectively. The S atom of an NCS group is also disordered over two positions with the fractional occupancies of 0.56576(02) and 0.43424(02) for S2A and