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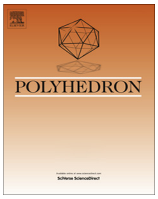

# Thiocyanate manganese(II) and cobalt(II) complexes of bis(pyrazol-1-yl)methane and bis(3,5-dimethylpyrazol-1-yl) methane – Syntheses, spectroscopic characterization, X-ray structure and magnetic properties

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ABSTRACT

Five novel thiocyanate complexes [Mn(bpzm)$_2$(NCS)$_2$] (**1**), [Mn(bdmpzm)$_2$(NCS)$_2$] (**2**), [Co(bpzm)$_2$(NCS)$_2$] (**3**), [Co(bdmpzm)$_2$(NCS)$_2$] (**4**) and [Co(bdmpzm)(NCS)$_2$] (**5**) (bpzm = bis(pyrazol-1-yl)methane and bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane) were synthesized and characterized structurally (by single X-ray analysis) and spectroscopically. The studies showed influence of central metal ion and organic co-ligands on the geometry of the thiocyanate Co(II) and Mn(II) complexes. Variable-temperature magnetic susceptibility measurements revealed occurrence of ferromagnetic interactions in **1** and the antiferromagnetic ones for the remaining complexes. The fluorescence properties of the Co(II) complexes were examined in solution and compared with the free ligands.

## 1. Introduction

Bis(pyrazol-1-yl)alkanes are neutral ligands containing two pyrazole cycles linked by an aliphatic spacer. They are related in concept to the heteroscorpionate ligands. Although they do not have a third donor group that can bond to the metal center, the third substituent on the carbon bridgehead may display significant interaction with either the metal center or other ligands bonded to the metal center. It is referred as heteroscorpionate ligand effect. The coordination properties of bis(pyrazol-1-yl)alkanes may be varied in wide range by introducing substituents into the pyrazole rings as well as by the flexibility of the space. Generally, two major coordination modes can be expected for bis(pyrazol-1-yl)alkanes, namely bidentate chelating and bidentate bridging. Bis(pyrazol-1-yl)methanes and 1,2-bis(pyrazol-1-yl)ethanes usually act as bidentate chelating ligands forming boat-shaped six- and seven-membered rings, respectively. 1,3-Bis(pyrazol-1-yl)propane forms eight-membered metallocycles or acts as a bidentate bridging ligand, whereas bis(pyrazol-1-yl)alkanes with four and more methylene groups in the spacer coordinate in a bridging mode giving coordination compounds of intriguing architectures and topologies [1].

On the other hand, thiocyanate ions are versatile ligands that can bind transition metal ions in a variety of ways. Having two different donor atoms can coordinate to metals through either the nitrogen or the sulfur atom, or both. Thus, these anions can act as both monodentate and bridging ligands leading to the formation of mononuclear and polynuclear species. The degree of nuclearity in the resulting complexes depends largely on the nature of the coordinated co-ligands and to some extent on the nature of the central metal ion, its oxidation state and the geometry of the complex. Transition metal complexes incorporating bridging thiocyanate ligands are in the center of interest due to their magnetic properties resulting from the ability of NCS$^-$ ions to propagate the magnetic interaction between the paramagnetic centers [2].

Recently we reported the results of our studies on two copper(II) coordination polymers of bis(pyrazol-1-yl)methane, $\{[Cu(bpzm)(SCN)][Cu(bpzm)(MeOH)][Cu(SCN)_4]\}_n$ and $[Cu_2(bpzm)_2(\mu\text{-}SCN)(SCN)_3]_n$ [3]. The first one belongs to a relatively scarce group of mixed-valence Cu$^{II}$/Cu$^{I}$ coordination polymers with

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interesting polymeric architecture. It creates infinite two-dimensional structure consisting of layers extending along crystallographic (001), in which the cations $[Cu^{II}(bpzm)(SCN)]^+$ and $[Cu^{II}(bpzm)(MeOH)]^{2+}$ are connected by ions $[Cu^{I}(SCN)_4]^{3-}$ through single end-to-end thiocyanato bridges. Structure $[Cu_2(bpzm)_2(\mu\text{-}SCN)(SCN)_3]_n$ consists of a *zig-zag* chain extending along the crystallographic direction [001] and linear chain running along the crystallographic direction [010]. It prompts us to further systematic studies on thiocyanate 3d metal complex of bis(pyrazol-1-yl)methanes.

Here, we present synthesis, X-ray studies as well as spectroscopic and magnetic properties of manganese(II) complexes $[Mn(bpzm)_2(NCS)_2]$ (**1**), $[Mn(bdmpzm)_2(NCS)_2]$ (**2**), $[Co(bpzm)_2(NCS)_2]$ (**3**), $[Co(bdmpzm)_2(NCS)_2]$ (**4**) and $[Co(bdmpzm)(NCS)_2]$ (**5**) ((bpzm = bis(pyrazol-1-yl)methane and bdmpzm = bis(3,5-dimethylpyrazol-1-yl)methane) (Scheme 1). Due to the presence of four sterically hindered electron-donating methyl substituents in *bdmpzm*, the used ligands *bpzm and bdmpzm* differ in both electronic and steric requirements.

## 2. Experimental

### 2.1. Materials

Bis(pyrazol-1-yl)methane and bis(3,5-dimethylpyrazol-1-yl)methane were synthesized according to the literature methods [4]. The other reagents used to the synthesis were commercially available and were used without further purification.

### 2.2. Preparation of $[Mn(bpzm)_2(NCS)_2]$ (**1**)

$NH_4SCN$ (0.18 g, 2.40 mmol) was dissolved in methanol (20 ml) and slowly added to the methanolic solution of $Mn(NO_3)_2{\cdot}4H_2O$ (0.30 g; 1.20 mmol) and bis(pyrazol-1-yl)methane (0.34 g; 2.40 mmol) and stirred at room temperature for 12 h. The resulting solution was left to stand at room temperature. After a week, white single crystals of **1** were obtained from the filtrate. Yield: 70%.

*Anal.* Calc. for $C_{16}H_{16}MnN_{10}S_2$: C, 41.11; H, 3.45; N, 29.97. Found: C, 41.54; H, 3.53; N, 29.49%.

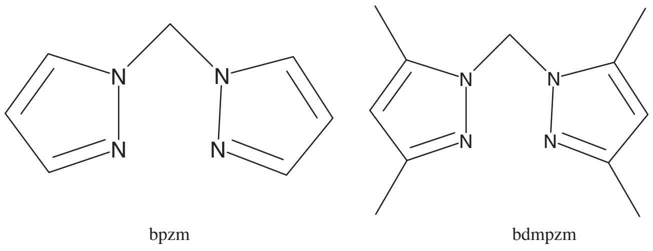
IR (KBr, $cm^{-1}$): 2082(vs) and 2054(vs) $\nu(C{=}N_{SCN})$; 1644(w), 1521(m) and 1510(m) $\nu(C{=}N_{bpzm})$ and $\nu(C{=}C_{bpzm})$; 778(s) and 772(s) $\nu(S{=}C_{SCN})$.

### 2.3. Preparation of $[Mn(bdmpzm)_2(NCS)_2]$ (**2**)

#### 2.3.1. Method A

A procedure similar to that for **1** was used with $NH_4SCN$ (0.18 g, 2.40 mmol), $Mn(NO_3)_2{\cdot}4H_2O$ (0.30 g; 1.20 mmol) and bis(3,5dimethylpyrazol-1-yl)methane (0.42 g; 2.40 mmol). After a few days white crystals of **2a** were collected by filtration in 60% yield.

*Anal.* Calc. for $C_{24}H_{32}MnN_{10}S_2$: C, 49.73; H, 5.56; N, 24.16. Found: C, 49.98; H, 5.72; N, 24.54%.



**Scheme 1.** Ligands investigated in this study.

IR (KBr, $cm^{-1}$): 2054(vs) $\nu(C{=}N_{SCN})$; 1620(w) and 1560(m) $\nu(C{=}N_{bdmpzm})$ and $\nu(C{=}C_{bdmpzm})$; 680(s) and 677(s) $\nu(S{=}C_{SCN})$.

#### 2.3.2. Method B

A procedure similar to that for **1** was used with $NH_4SCN$ (0.19 g, 2.44 mmol), $Mn(CH_3COO)_2{\cdot}4H_2O$ (0.30 g; 1.22 mmol) and bis(3,5-dimethylpyrazol-1-yl)methane (0.42 g; 2.44 mmol). White single crystals of **2b** were collected in 65% yield after a week.

*Anal.* Calc. for $C_{24}H_{32}MnN_{10}S_2$: C, 49.73; H, 5.56; N, 24.16. Found: C, 49.86; H, 5.48; N, 24.69%.

IR (KBr, $cm^{-1}$): 2059 (vs) $\nu(C{=}N_{SCN})$; 1615(w) and 1560(m) $\nu(C{=}N_{bdmpzm})$ and $\nu(C{=}C_{bdmpzm})$; 680(s) and 677(s) $\nu(S{=}C_{SCN})$.

### 2.4. Preparation of $[Co(bpzm)_2(NCS)_2]$ (**3**)

$NH_4SCN$ (0.19 g, 2.52 mmol) was dissolved in methanol (20 ml) and slowly added to the methanolic solution of $CoCl_2{\cdot}6H_2O$ (0.30 g; 1.26 mmol) and bis(pyrazol-1-yl)methane (0.37 g; 2.52 mmol) and stirred at room temperature for 12 h. After a week pink single crystals of **3** were collected in 70% yield.

*Anal.* Calc. for $C_{16}H_{16}CoN_{10}S_2$: C, 40.77; H, 3.42; N, 29.71. Found: C, 40.99; H, 3.54; N, 29.58%.

IR (KBr, $cm^{-1}$): 2070(vs) $\nu(C{=}N_{SCN})$; 1628(w) and 1514(m) $\nu(C{=}N_{bpzm})$ and $\nu(C{=}C_{bpzm})$; 768(s) and 731(s) $\nu(S{=}C_{SCN})$.

### 2.5. Preparation of $[Co(bdmpzm)_2(NCS)_2]$ (**4**) and $[Co(bdmpzm)(NCS)_2]$ (**5**)

A procedure similar to that for **3** was used with $NH_4SCN$ (0.19 g, 2.52 mmol), $CoCl_2{\cdot}6H_2O$ (0.3 g; 1.26 mmol) and bis(3,5-dimethylpyrazol-1-yl)methane (0.45 g; 2.52 mmol) and stirred at room temperature for 12 h. The resulting blue precipitate of **5** (the main product) was filtered off and dried in air. The resulting solution after filtration was left to stand at room temperature. After a few days, pale pink crystals of **4** were obtained from the filtrate. Single crystals of **5** suitable for X-ray structure determination were obtained by slow recrystallization from methanol. Yield of **4** 30%, yield of **5** 60%.

*Anal.* Calc. for $C_{24}H_{32}CoN_{10}S_2$: C, 49.39; H, 5.53; N, 24.00. Found: C, 49.85; H, 5.66; N, 24.45%.

IR of **4** (KBr, $cm^{-1}$): 2093(vs) and 2074 (vs) $\nu(C{=}N_{SCN})$; 1629 (w) and 1565 (s) $\nu(C{=}N_{bdmpzm})$ and $\nu(C{=}C_{bdmpzm})$; 813(s) and 801(s) $\nu(S{=}C_{SCN})$.

IR of **5** (KBr, $cm^{-1}$): 2069(vs) $\nu(C{=}N_{SCN})$; 1654 (w) and 1553 (s) $\nu(C{=}N_{bdmpzm})$ and $\nu(C{=}C_{bdmpzm})$; 695(s) $\nu(S{=}C_{SCN})$.

*Anal.* Calc. for $C_{13}H_{16}CoN_6S_2$: C, 41.16; H, 4.25; N, 22.15. Found: C, 41.51; H, 4.36; N, 22.61%.

### 2.6. Crystal structures determination and refinement

The X-ray intensity data of **1**–**5** were collected on a Gemini A Ultra diffractometer equipped with Atlas CCD detector and graphite monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) at room temperature. Details concerning crystal data and refinement are given in Table 1. Lorentz, polarization and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm [5] were applied. The structures were solved by the direct methods and subsequently completed by the difference Fourier recycling. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique. The hydrogen atoms were treated as "riding" on their parent carbon atoms and assigned isotropic temperature factors equal 1.2 (aromatic) and 1.5 (water) times the value of equivalent temperature factor of the parent atom. The methyl groups were allowed to rotate about their local threefold axis. SHELXS97 and SHELXL97 [6] programs were used for all the calculations. Atomic scattering factors were those