

# Dinuclear $[\text{Co}^{\text{II}}(\text{NCMe})_5\text{Co}^{\text{II}}(\text{NCS})_4]$ Possessing Octahedral and Tetrahedral $\text{Co}^{\text{II}}$ Sites

Endrit Shurdha,<sup>†</sup> Curtis E. Moore,<sup>‡</sup> Arnold L. Rheingold, and Joel S. Miller<sup>\*†</sup>

<sup>†</sup>Department of Chemistry, University of Utah, Salt Lake City, Utah 84112-0850, United States

<sup>‡</sup>Department of Chemistry, University of California, San Diego, La Jolla, California 92093-0358, United States

**S** Supporting Information

**ABSTRACT:** The structural and magnetic properties of dinuclear  $[\text{Co}^{\text{II}}(\text{NCMe})_5\text{Co}^{\text{II}}(\text{NCS})_4] \cdot \text{MeCN}$  have been investigated. The structure consists of an octahedral  $\text{Co}^{\text{II}}(\text{NCMe})_5$  center connected to a tetrahedral  $\text{Co}^{\text{II}}(\text{NCS})_4$  center bridged by a  $\mu_{1,3}\text{-NCS}^-$  ligand. The bridging  $\text{NCS}^-$  weakly couples the pair of  $S = 3/2$   $\text{Co}^{\text{II}}$  spin sites, as evidenced by the magnetic data being best fit by the Curie–Weiss expression with  $\theta = -15.5$  K.

Thiocyanate is well established as both a terminal ligand and a multidentate ligand for the construction of coordination complexes<sup>1</sup> and has led to network structures with extended bonding in one, two,<sup>2</sup> and/or three<sup>3</sup> dimensions. In addition, mixed-metal systems<sup>4</sup> have been reported with thiocyanate bridging. Because of the facile loss of the thiocyanate ligand, as well as its ability to reduce tetracyanoethylene (TCNE) to  $[\text{TCNE}]^{\bullet-}$ , we have studied this chemistry with the goal of making new organic-based magnets.<sup>5</sup>

As part of these studies, we report a dicobalt(II) complex of  $[\text{Co}_2^{\text{II}}(\text{NCMe})_6(\text{NCS})_4]$  (**1**) composition with each  $\text{Co}^{\text{II}}$  site in a different geometry, namely, one octahedral and one tetrahedral. In an attempt to prepare  $[\text{Co}^{\text{II}}(\text{NCS})_2(\text{NCMe})_2]$ , which was expected to be isostructural with chain-structured  $[\text{M}^{\text{II}}(\text{NCS})_2(\text{OCMe}_2)_2]$  ( $\text{M} = \text{Cr}, \text{Mn}, \text{Fe}$ ),<sup>5</sup>  $\text{Co}(\text{NCS})_2$  (100 mg) was dissolved in acetonitrile, which formed a blue solution. Upon cooling at  $-20$  °C for 24 h, purple crystals of **1** formed and were collected via filtration. **1** has unexpected IR absorptions at (a) 2311 and 2284  $\text{cm}^{-1}$ , which suggest coordinated acetonitrile,<sup>6</sup> (b) 2254  $\text{cm}^{-1}$  indicative of uncoordinated acetonitrile, (c) 2139  $\text{cm}^{-1}$  as a sharp peak, and (d) 2073  $\text{cm}^{-1}$ , suggesting a bridging<sup>7</sup> and an N-bound terminal isothiocyanate, respectively.<sup>8</sup>

The structure<sup>9</sup> of **1** consists of one octahedral  $\text{Co}^{\text{II}}$  center coordinated to five acetonitriles and an S-bound  $\mu_{1,3}\text{-NCS}$  ligand. The second  $\text{Co}^{\text{II}}$  is tetrahedral with three N-bound isothiocyanate ligands and the aforementioned bridging N-bound  $\mu_{1,3}\text{-NCS}$  ligand (Figure 1). In addition, one acetonitrile molecule is not coordinated, in accordance with the IR spectrum. Hence, its composition is  $[\text{Co}^{\text{II}}(\text{NCMe})_5\text{Co}^{\text{II}}(\text{NCS})_4] \cdot \text{MeCN}$  or  $[\text{Co}^{\text{II}}(\text{NCMe})_5\text{-}\mu_{1,3}\text{-SCN-Co}^{\text{II}}(\text{NCS})_3] \cdot \text{MeCN}$ .

The five terminal  $\text{Co}-\text{NCMe}$  bond lengths of mean 2.107 Å [range 2.090(2)–2.123(2) Å] for the octahedral  $\text{Co}^{\text{II}}$  center agree with that of 2.114(7) Å in  $[\text{Co}(\text{NCMe})_6]^{2+}$ .<sup>10</sup> The shorter mean of 1.951 Å [range 1.949(2)–1.972(2) Å] for the three terminal  $\text{Co}-\text{NCS}$  bond lengths of the tetrahedral  $\text{Co}^{\text{II}}$  center compare closely with that of 1.973(3) Å in  $[\text{Co}(\text{NCS})_4]^{2+}$ .<sup>11</sup> For

the bridged  $\text{NCS}$  ligand, the observed  $\text{Co}-\text{NCS}$  and  $\text{Co}-\text{SCN}$  bond lengths do not expectedly suggest any appreciable charge transfer within the bridging  $\text{NCS}$  motif; the bridging  $\text{Co}-\text{NCS}$  distance is only 0.02 Å longer than that for the three terminal  $\text{Co}-\text{NCS}$  distances, and the bridging  $\text{Co}-\text{SCN}$  distance is not significantly different from that of 2.575(43) Å in  $\text{Co}(\text{NCS})_2 \cdot (\text{C}_6\text{H}_5\text{NO}_2)_2$ .<sup>12</sup> The intradimer distance between the two cobalt centers is 5.732(2) Å, while the shortest interdimer distance is 5.319(2) Å. The intradimer distance is comparable to other dinuclear cobalt species bridged by thiocyanate, e.g.,  $[\text{Co}_2(\text{NCS})_2(\text{H}_2\text{O})_2(\text{C}_7\text{H}_3\text{NO}_4)_2]$  [5.590(1) Å].<sup>13</sup>

Compounds that possess tetrahedral and octahedral centers are rare and are limited to tetrahedral  $\text{Hg}^{\text{II}}$  S-bound to a thiocyanate bridged to  $\text{M}^{\text{II}}$  ( $\text{M} = \text{Co}$ ,<sup>14</sup>  $\text{Ni}$ ,<sup>15</sup>) forming two-dimensional layers with the  $\mu_{1,3}\text{-NCS}$  motif. To the best of our knowledge, **1** is the only dinuclear complex with tetrahedral and octahedral geometries in its structure.

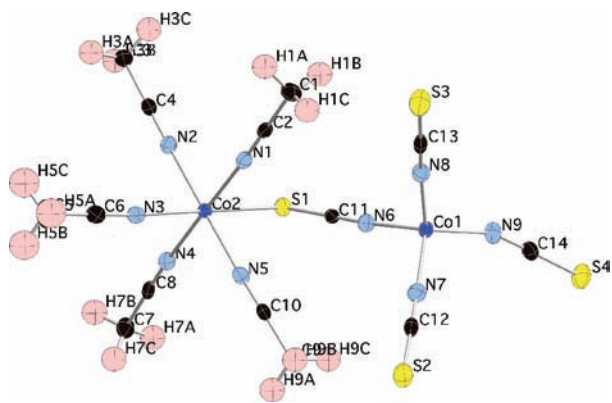
The magnetic susceptibility,  $\chi$ , of **1** was measured between 5 and 300 K.<sup>16</sup> The 300 K  $\chi T(T)$  value is 5.575  $\text{emu} \cdot \text{K}/\text{mol}$  and is higher than the spin-only expectation of 3.75  $\text{emu} \cdot \text{K}/\text{mol}$  for two  $S = 3/2$  sites.  $\chi T(T)$  gradually decreases with decreasing temperature until  $\sim 5$  K, characteristic of paramagnetic systems with small coupling. The magnetic data were modeled by expressions for (a) independent spins antiferromagnetically coupled ( $\theta$ ) for two  $S = 3/2$   $\text{Co}^{\text{II}}$  sites with the Curie–Weiss equation (eq 1), (b) the inclusion of zero field splitting,  $D$ , for this independent spin model (eq 2),<sup>17</sup> and (c) strong intradimer coupling with the dinuclear  $S = 3/2 \pm 3/2$  Bleaney–Bowers-like equation (eq 2). For all three equations,  $N$  is Avogadro's number,  $\mu_{\text{B}}$  is the Bohr magneton,  $g$  is the Landé value,  $k_{\text{B}}$  is Boltzmann's constant, and  $S$  is the total spin quantum number.

$$\chi = 2 \left[ \frac{N\mu_{\text{B}}^2 g_{\text{avg}}^2}{3k_{\text{B}}(T - \theta)} S(S + 1) \right] \quad (1)$$

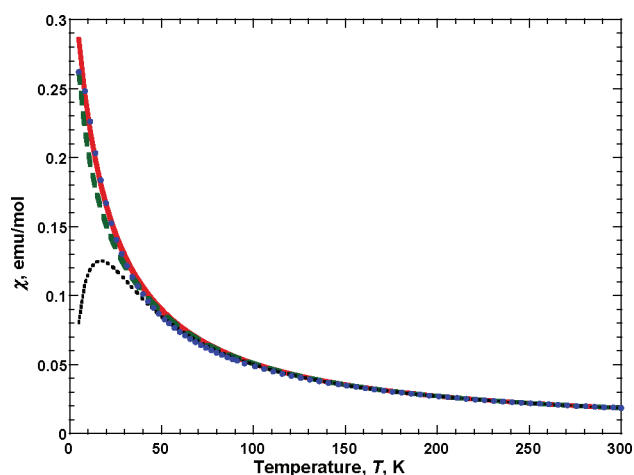
$$\chi = \left[ \frac{1}{3} \frac{N\mu_{\text{B}}^2 g^2 S(S + 1)}{mk_{\text{B}}(T - \theta)} \left( \frac{1 + 9e^{-2D/k_{\text{B}}T}}{4 + (1 + e^{-2D/k_{\text{B}}T})} \right) + \frac{2}{3} \frac{N\mu_{\text{B}}^2 g^2 S(S + 1)}{mk_{\text{B}}(T - \theta)} \left( \frac{1 + \frac{3T}{4D}(1 - e^{-2D/k_{\text{B}}T})}{1 + e^{-2D/k_{\text{B}}T}} \right) \right] \quad (2)$$

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**Figure 1.** ORTEP atom-labeling diagram (50% probability thermal ellipsoids) of **1**.



**Figure 2.**  $\chi(T)$  data (●) of  $[\text{Co}(\text{NCMe})_5\text{Co}(\text{NCS})_4] \cdot \text{MeCN}$  and Curie–Weiss (—), zero-field-splitting (---), and Bleaney–Bowers (···) fitting expressions.

$$\chi = \left[ \frac{N\mu_B^2 g^2 S(S+1)}{3k_B(T-\theta)} \right] \left[ \frac{2e^{2J/k_B T} + 10e^{6J/k_B T} + 28e^{12J/k_B T}}{1 + 3e^{2J/k_B T} + 5e^{6J/k_B T} + 7e^{12J/k_B T}} \right] + \text{TIP} \quad (3)$$

The  $\chi(T)$  data can be well fit for all temperatures by the Curie–Weiss expression (eq 1), with  $g_{\text{avg}} = 2.5$  and  $\theta = -15.5$  K in accordance with other octahedral and tetrahedral cobalt(II) complexes (Figure 2).<sup>18</sup> The negative  $\theta$  value indicates antiferromagnetic coupling. This is the best fit compared to the other two models commonly used for related cobalt(II) complexes, namely, inclusion of zero field splitting,  $D$  (eq 2), or a dinuclear Bleaney–Bowers-like equation for two  $S = 3/2$  spin sites that includes temperature-independent paramagnetism (TIP; eq 3). Above 27 K, the  $\chi(T)$  data can be fit with eq 2 with the parameters  $g_{\text{avg}} = 2.07$ ,  $D/k_B = 35$  K, and  $\theta = -6$  K. The  $D$  parameter for this dinuclear complex is comparable to those for one-dimensional chains of  $[\text{Co}(\mu\text{-SO}_4)(3\{\text{S}\}\text{-tert-butylpyrazole})_3]$  reported in the literature.<sup>19</sup> Because of the dinuclear structure, eq 3 was identified to be a plausible model for the data, but the data only fit above 40 K ( $g = 2.48$ ,  $J/k_B = -5$  K,  $\theta = -1$ , and  $\text{TIP} = 200 \times 10^{-6}$  emu). The coupling parameters for the dinuclear complex indicate antiferromagnetic coupling within the dinuclear

species. Hence, the best fit for the dinuclear cobalt complex is the Curie–Weiss expression.

$[\text{Co}^{\text{II}}(\text{NCMe})_5\text{Co}^{\text{II}}(\text{NCS})_4] \cdot \text{MeCN}$  is a good synthetic precursor because of the ease at which the  $\text{NCS}^-$  and MeCN ligands are lost. The reaction of  $[\text{Co}^{\text{II}}(\text{NCMe})_5\text{Co}^{\text{II}}(\text{NCS})_4] \cdot \text{MeCN}$  with  $(\text{NBu}_4)^+[\text{TCNE}]^{\bullet-}$  in  $\text{CH}_2\text{Cl}_2$  has led to the formation of  $[\text{Co}^{\text{II}}(\text{TCNE})[\text{C}_4(\text{CN})_8]_{1/2}] \cdot z\text{CH}_2\text{Cl}_2$ .<sup>5,20</sup>

## ASSOCIATED CONTENT

**S Supporting Information.** Single-crystal X-ray crystallographic CIF file for **1** (CCDC 840142). This material is available free of charge via the Internet at <http://pubs.acs.org>. The atomic coordinates for this structure have also been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [jsmiller@chem.utah.edu](mailto:jsmiller@chem.utah.edu).

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correction for the diamagnetic contribution from the sample holder, the core diamagnetic corrections of  $-315 \times 10^{-6}$  emu/mol of Co was used.

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(20)  $[\text{Co}(\text{NCMe})_5\text{Co}(\text{NCS})_4] \cdot \text{MeCN}$  was reacted with 2 equiv of  $(\text{NBu}_4)(\text{TCNE})$  in dichloromethane for 5 days. The brown precipitate of  $\text{Co}^{\text{II}}(\text{TCNE})[\text{C}_4(\text{CN})_8]_{1/2} \cdot z\text{CH}_2\text{Cl}_2$  [IR (KBr):  $\nu_{\text{CN}} = 2229$  (m), 2186 (sh), 2173 (b)] was isolated via filtration.