

## Three Cyanide-Bridged One-Dimensional Single Chain Co<sup>III</sup>-Mn<sup>II</sup> Complexes: Rational Design, Synthesis, Crystal Structures and Magnetic Properties

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Two pyridinecarboxamide dicyanidecobalt(III) building blocks and two mononuclear seven-coordinated macrocycle manganese(II) compounds have been rationally selected to assemble cyanide-bridged hetero-bimetallic complexes, resulting in three cyanide-bridged Co<sup>III</sup>-Mn<sup>II</sup> complexes. Single X-ray diffraction analysis show that these complexes {[Mn(L<sup>1</sup>)]Co(bpb)}ClO<sub>4</sub>·CH<sub>3</sub>OH·0.5H<sub>2</sub>O (**1**), {[Mn(L<sup>2</sup>)]Co(bpb)}ClO<sub>4</sub>·0.5CH<sub>3</sub>OH (**2**) and {[Mn(L<sup>1</sup>)]Co(bpmb)}ClO<sub>4</sub>·H<sub>2</sub>O (**3**) (L<sup>1</sup> = 3,6-diazaoctane-1,8-diamine, L<sup>2</sup> = 3,6-dioxaoctano-1,8-diamine; bpb<sup>2-</sup> = 1,2-bis(pyridine-2-carboxamido)benzenate, bpmb<sup>2-</sup> = 1,2-bis(pyridine-2-carboxamido)-4-methyl-benzenate) all present predictable one-dimensional single chain structures. The molecular structures of these one-dimensional complexes consists of alternating units of [Mn(L)]<sup>2+</sup> (L = L<sup>1</sup> or L<sup>2</sup>) and [Co(L')(CN)<sub>2</sub>]<sup>-</sup> (L' = bpb<sup>2-</sup>, or bpmb<sup>2-</sup>), forming a cyanide-bridged cationic polymeric chain with free ClO<sub>4</sub><sup>-</sup> as the balance anion. The coordination geometry of manganese(II) ion in the three one-dimensional complexes is a slightly distorted pentagonal-bipyramidal with two cyanide nitrogen atoms at the *trans* positions and N<sub>5</sub> or N<sub>3</sub>O<sub>2</sub> coordinating mode at the equatorial plane from ligand L<sup>1</sup> or L<sup>2</sup>. Investigation over magnetic properties of these complexes reveals that the very weak magnetic coupling between neighboring Mn(II) ions connected by the diamagnetic dicyanidecobalt(III) building block. A best-fit to the magnetic susceptibility of complex **1** leads to the magnetic coupling constants  $J = -0.084(3) \text{ cm}^{-1}$ .

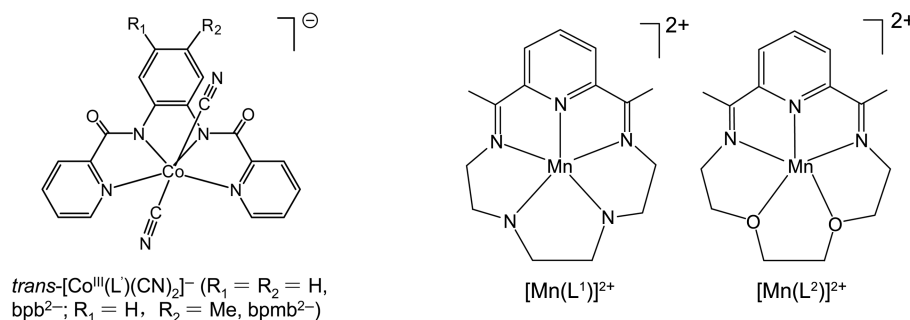
**Key Words** : Cyanide-bridged, Heterometallic complex, Crystal structure, Magnetic property

### Introduction

During the past three decades, the design and synthesis of molecular magnetic materials has been given extensive attention due to their potential application in several scientific fields,<sup>1-3</sup> including chemistry, physics, materials and biology, *etc.* Recently, the design and synthesis of low-dimensional cyanide-bridged magnetic complexes has attracted much interest because of the necessity for the full and clear elucidation of magneto-structural correlation, and the preparation of some interesting molecular magnetic materials such as spin crossover materials,<sup>4,5</sup> and single-molecule magnets (SMMs)<sup>6,7</sup> as well as single-chain magnets (SCMs).<sup>8,9</sup> Because many effect factors can play important role in the forming process of the cyanide-bridged complexes with desirable molecular structures, there still face a huge challenge for the

directional design and synthesis of cyanide-bridged compounds, although many cyanide-bridged low-dimensional magnetic compounds have been synthesized up to date.

We have designed and synthesized many low-dimensional cyanide-bridged complexes with various structures by rationally using a series of rigid *trans*-dicyanide-containing building blocks based on pyridinecarboxamide ligands,<sup>10</sup> in which these relatively large equatorial in-plane ligands can efficiently decrease the dimensions of the complexes formed and weaken the intermolecular magnetic coupling. Due to the diamagnetic nature of Co(III) ion, the cyanide precursors containing the Co(III) ion have rarely been used in the preparation of cyanide-bridged magnetic complexes. In this paper, we report the design, synthesis, crystal structures and magnetic properties of three cyanide-bridged one-dimensional Co<sup>III</sup>-Mn<sup>II</sup> heterometallic complexes with the formula



Scheme 1

{[Mn(L<sup>1</sup>)]Co(bpb)}ClO<sub>4</sub>·CH<sub>3</sub>OH·0.5H<sub>2</sub>O (**1**), {[Mn(L<sup>2</sup>)]Co(bpb)}ClO<sub>4</sub>·0.5CH<sub>3</sub>OH (**2**) and {[Mn(L<sup>1</sup>)]Cobpmb}ClO<sub>4</sub>·H<sub>2</sub>O (**3**) based on two dicyanidecobalt(III) building blocks and two seven-coordinated macrocyclic manganese (II) compounds (Scheme 1).

### Experimental

Elemental analyses of carbon, hydrogen, and nitrogen were carried out with an Elementary Vario El instrument. IR spectra of KBr pellets were recorded on a Magna-IR 750 spectrophotometer in the 4000–400 cm<sup>-1</sup> region. Variable-temperature magnetic susceptibility and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

All the reactions were carried out under air atmosphere and all chemicals and solvents used were reagent grade without further purification. K[Co<sup>III</sup>(bpb)(CN)<sub>2</sub>] [bpb<sup>2-</sup> = 1,2-bis(pyridine-2-carboxamido)benzenate] and its analogue were synthesized as described in the literature.<sup>11</sup> [Mn(L<sup>1</sup>)(H<sub>2</sub>O)Cl]ClO<sub>4</sub> and [Mn(L<sup>2</sup>)(H<sub>2</sub>O)Cl]ClO<sub>4</sub> was synthesized according to our recent report.<sup>12</sup>

**Synthesis of the Complexes 1-3.** These three complexes were prepared by a similar method, therefore only the synthesis of complex **1** was described in detail. To a solution of [Mn(L)(H<sub>2</sub>O)Cl]ClO<sub>4</sub> (48.1 mg, 0.1 mmol) in methanol (10 mL), K[Co(bpb)(CN)<sub>2</sub>] (0.10 mmol, 46.3 mg) dissolved in methanol/water (4:1, v:v) (10 mL) was carefully added. The resulting mixture was filtered at once and the filtrate kept undisturbed at room temperature. After one week, brown-black block crystals were collected by filtration with the yield of 51.1 mg, 57%. Anal. Calcd. for C<sub>36</sub>H<sub>39</sub>ClCoMnN<sub>11</sub>O<sub>7.5</sub>: C, 48.30; H, 4.39; N, 17.21. Found: C, 48.48; H, 4.30; N, 17.41. Main IR bands (cm<sup>-1</sup>): 2120 (s, νC≡N), 1098 (vs, νCl=O).

**Complex 2:** Yield: 49.5 mg, 56.1%. Anal. Calcd. for C<sub>35.5</sub>H<sub>36</sub>ClCoMnN<sub>9</sub>O<sub>9</sub>: C, 48.34; H, 4.11; N, 14.29. Found: C, 48.28; H, 4.04; N, 14.42. 2117 (s, νC≡N), 1100 (vs, νCl=O).

**Complex 3:** Yield: 43.5 mg, 49.1%. Anal. Calcd. for C<sub>36</sub>H<sub>39</sub>ClCoMnN<sub>11</sub>O<sub>7</sub>: C, 48.74; H, 4.43; N, 17.37. Found: C, 48.59; H, 4.35; N, 16.95. 17.51. (s, νC≡N), 2119 (s, νC≡N), 1095 (vs, νCl=O).

**X-ray Data Collection and Structure Refinement.** Crystal data and structure refinement details for complexes **1-3** are listed in Tables 1. Crystal data were collected on a Bruker SMART CCD diffractometer with a MoKα sealed tube (λ = 0.71073 Å) at 293 K, using a ω scan mode. The structure was solved by a combination of direct method and heavy atom method using SHELXL97. All the nonhydrogen atoms were refined with anisotropic displacement coefficients. For the disordered contents, the partially occupied atoms were refined isotropically. Hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(C) and their coordinates were allowed to ride on their respective carbons using SHELXL97 except some of the H atoms of the solvent molecules. These H atoms were refined isotropically with fixed U values and the DFIX command was used to rationalize the bond parameter. CCDC 863854, 863855 and 863856 for complexes **1-3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

### Results and Discussion

**Synthesis and General Characterization.** As shown in Scheme 1, the 15-membered pentadentate macrocycles L<sup>1</sup> and L<sup>2</sup> (L<sup>1</sup> = 3,6-diazoctane-1,8-diamine, L<sup>2</sup> = 3,6-dioxaoctano-1,8-diamine) have been found to adopt a planar conformation, imposing a pentagonal-based geometry on the

**Table 1.** Crystallographic data for complexes **1-3**

|   | <b>1</b>   | <b>2</b>  | <b>3</b>   |
|---|--|---|--|
| Chemical formula                                    | C <sub>36</sub> H <sub>39</sub> ClCoMnN <sub>11</sub> O <sub>7.5</sub> | C <sub>35.5</sub> H <sub>36</sub> ClCoMnN <sub>9</sub> O <sub>9</sub> | C <sub>36</sub> H <sub>39</sub> ClCoMnN <sub>11</sub> O <sub>7</sub> |
| Fw  | 895.10   | 882.05  | 887.10   |
| crystal system                                      | monoclinic   | monoclinic  | monoclinic   |
| Space group   | <i>P2(1)/c</i>   | <i>P2(1)/n</i>  | <i>P2(1)/c</i>   |
| <i>a</i> /Å   | 11.4258(4)   | 19.845(15)  | 11.469(3)  |
| <i>b</i> /Å   | 17.8126(5)   | 17.581(14)  | 17.759(4)  |
| <i>c</i> /Å   | 20.3436(6)   | 22.370(18)  | 20.278(5)  |
| α/deg   | 90   | 90  | 90   |
| β/deg   | 99.634(2)  | 95.424(16)  | 98.897(5)  |
| γ/deg   | 90   | 90  | 90   |
| <i>V</i> /Å <sup>3</sup>                            | 4082.0(2)  | 7770(11)  | 4080.7(16)   |
| <i>Z</i>  | 4  | 8   | 4  |
| <i>F</i> (000)                                      | 1844   | 3624  | 1828   |
| <i>GOF</i>  | 1.025  | 1.014   | 1.035  |
| <i>R</i> <sub>1</sub> [ <i>I</i> > 2 σ( <i>I</i> )] | 0.0706   | 0.0788  | 0.0754   |
| <i>wR</i> <sub>2</sub> (all data)                   | 0.2244   | 0.2483  | 0.2519   |

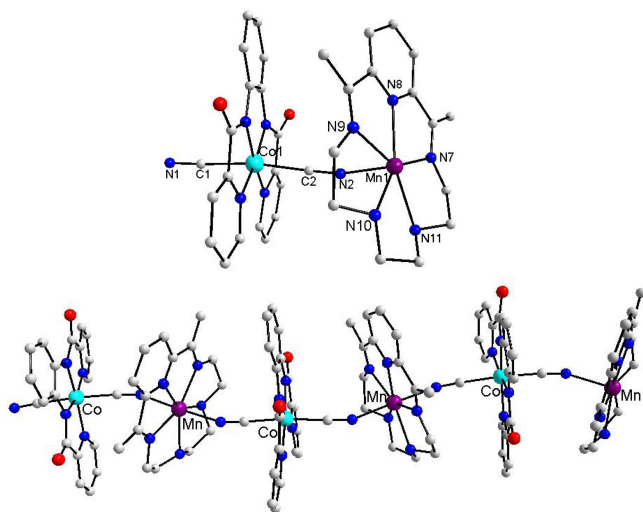
central metal ion with different electronic configuration, leading to the stabilization of seven-coordinated species. Because of the large steric effect coming from the macrocyclic ligand and the existence of two weakly bonded and replaceable ligands at the two *trans* positions, these two seven-coordinated Mn(II) compounds are the one of the most excellent precursors for the design and synthesis of low-dimensional complexes.<sup>13-16</sup>

As suggested by our recent works, pyridinecarboxamide *trans*-dicyanidemetalate building blocks with relative large planar equatorial pyridinecarboxamido ligand and two *trans* cyanide groups are good candidates for the preparation of low-dimensional cyanide-bridged complexes with various structures.<sup>10</sup> As a consequence, reaction of  $[\text{Co}(\text{L}')(\text{CN})_2]^-$  with the above mentioned macrocyclic manganese(II) precursors might result in complexes with expected one-dimensional cyanide-bridged single chain structure due to the suitable steric effect of peripheral organic ligands, active reacting sites, and charge of these two building blocks.

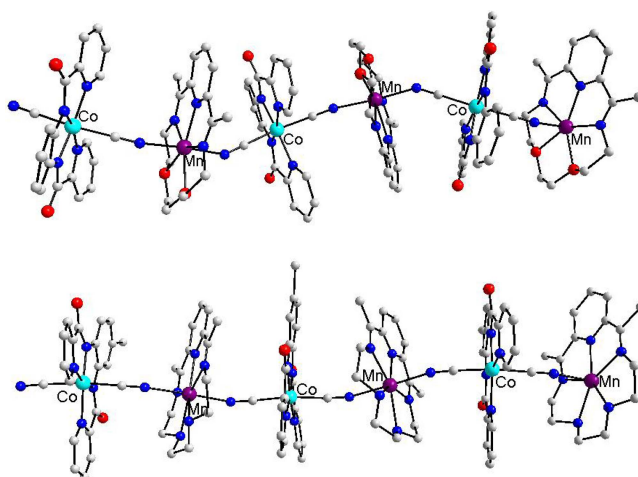
All the three cyanide-bridged complexes have been characterized by IR spectra. In the IR spectra of complexes 1-3, the single peak at about  $2120\text{ cm}^{-1}$  can be assigned to the bridging cyanide groups. Observation of a strong broad peak centered at *ca.*  $1100\text{ cm}^{-1}$  suggests the presence of  $\text{ClO}_4^-$  anions.

**Crystal Structures of Complexes 1-3.** The selected bond lengths and angles for complexes 1-3 are given in Table 2. For complex 1, its asymmetry cationic unit and one-dimensional cationic chain structures are shown in Figure 1. For 2 and 3, their one-dimensional cationic chain structures are given in Figure 2. The representative cell packing diagram for complexes 1-3 is depicted in Figure 3.

As shown in Figures 1 and 2, these three complexes possess expected one-dimensional cationic single chain structure comprising of repeated  $[-\text{NC}-\text{Co}(\text{L}')-\text{CN}-\text{Mn}(\text{L})-]$  units with  $\text{ClO}_4^-$  acting as balance anion. In complexes 1-3, each *trans*-dicyanide-containing building block, acting as a



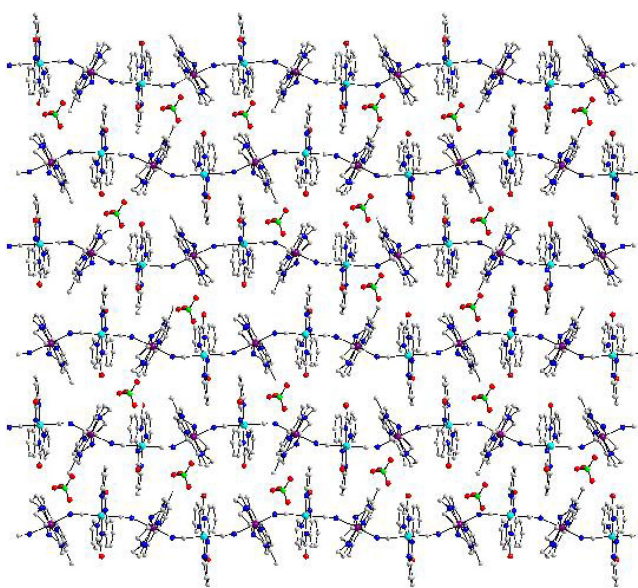
**Figure 1.** The asymmetry cationic unit and one-dimensional cationic chain structure of complex 1. All the hydrogen atoms, free  $\text{ClO}_4^-$ , and solvent molecules have been omitted for clarity.



**Figure 2.** The one-dimensional cationic chain structure of complexes 2 (top) and 3 (bottom). All the hydrogen atoms, free  $\text{ClO}_4^-$ , and solvent molecules have been omitted for clarity.

bidentate ligand through its two cyanide groups, connects the Mn(II) ion of two independent macrocyclic manganese units. The Co atom is coordinated by four N atoms of cyanide-containing precursor locating in the equatorial plane and two C atoms of cyanide groups in *trans* position, forming a slightly distorted octahedral geometry, which have been proven by the bond lengths around the Co ion (Table 2). As can be found in Table 2, the bond angle of  $\text{Co}-\text{C}\equiv\text{N}$  in the realm of  $173.2(6)-176.1(11)^\circ$  clearly indicates that the three atoms are in a good linear configuration.

The Mn(II) ion in complexes 1-3 is seven-coordinated, forming a slightly distorted pentagonal-bipyramidal coordination geometry, in which the five equatorial positions are occupied by  $\text{N}_5$  or  $\text{N}_3\text{O}_2$  unit coming from the macrocyclic ligand and two axial ones coordinated by two N atoms of



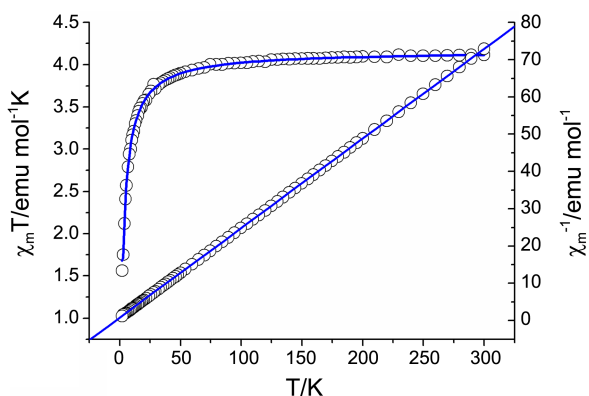
**Figure 3.** The representative cell packing diagram for complexes 1-3 along a axis. All the hydrogen atoms have been omitted for clarity.

**Table 2.** Selected bond lengths (Å) and angles (°) for complexes **1-3**

|                | <b>1</b> | <b>2</b> | <b>3</b>  |
|----------------|----------|----------|-----------|
| Mn1-N1         | 2.266(4) | 2.214(7) | 2.234(10) |
| Mn1-N2         | 2.245(4) | 2.203(6) | 2.260(10) |
| Mn(1)-N(7)     | 2.230(7) | 2.187(6) | 2.228(17) |
| Mn(1)-N(8)     | 2.293(6) | 2.214(7) | 2.331(18) |
| Mn(1)-N(9)     | 2.328(6) | 2.205(7) | 2.349(16) |
| Mn(1)-N(10)/O3 | 2.356(7) | 2.234(5) | 2.309(13) |
| Mn(1)-N(11)/O4 | 2.316(7) | 2.243(6) | 2.230(13) |
| Co1-C1         | 1.922(5) | 1.898(7) | 1.906(13) |
| Co 1-C2        | 1.926(5) | 1.899(7) | 1.913(13) |
| Co 1-N3        | 1.896(5) | 1.862(6) | 1.894(10) |
| Co 1-N4        | 1.894(5) | 1.855(6) | 1.886(10) |
| Co 1-N5        | 1.975(5) | 1.938(6) | 1.972(11) |
| Co 1-N6        | 1.982(5) | 1.925(6) | 1.972(9)  |
| Mn1-N1-C1      | 165.0(4) | 165.9(6) | 155.2(9)  |
| C1-Co1-C2      | 177.1(2) | 177.6(3) | 177.9(5)  |
| Co1-C1-N1      | 175.5(5) | 176.1(7) | 174.9(11) |
| Co1-C2-N2      | 175.3(5) | 173.2(6) | 176.1(11) |

cyanide groups. The distances between Mn ion and equatorial N or O atoms, Table 2, are in good agreement with those found in its precursors.<sup>17,10c</sup> The average Mn-N<sub>cyanide</sub> bond lengths in these three complexes are 2.256, 2.209 and 2.247 Å, respectively, basically consistent with the Mn-N<sub>equatorial</sub> bond lengths. As tabulated in Table 2, the Mn-N≡C bond angles in complexes **1-3** are somewhat bent with the values of 165.0(4), 165.9(6), and 155.2(9)°, respectively.

**Magnetic Property of Complex 1.** Taking into account the structural similarity for these three complexes, the magnetic properties for complex **1** as typical representatives has been carried out. The temperature dependences of magnetic susceptibility for complex **1** measured in the temperature range of 2-300 K in the applied field of 2000 Oe are given in Figure 4. The  $\chi_m T$  value for complexes **1** at room temperature is 4.12 emu K mol<sup>-1</sup>, slightly lower than the spin only value of 4.375 emu K mol<sup>-1</sup> for the isolated high spin Mn(II) ( $S = 5/2$ ). With the temperature decreasing, the  $\chi_m T$  value remains almost constant from 300 to about



**Figure 4.** Temperature dependence of  $\chi_m T$  and  $\chi_m^{-1}$  of complex **1**. (The solid line represents the best fit based on the parameters discussed in the text).

50 K. After this, the  $\chi_m T$  value starts to decrease rapidly and reaches their lowest peak with the value of 1.70 emu K mol<sup>-1</sup> at 2 K. The magnetic susceptibility conforms well to Curie-Weiss law in a range of 2-300 K (the inset of Fig. 4) and gives the negative Weiss constant  $\theta = -3.16$  K and Curie constant  $C = 4.03$  emu K mol<sup>-1</sup>. These results primarily show the antiferromagnetic magnetic coupling between the two Mn(II) centers bridged by [-NC-Co(L)-CN-] unit in these complexes.

The magnetic data are analyzed by using the Hamiltonian:  $\hat{H} = -2\Sigma J\hat{S}_i\hat{S}_{i+1}$ . The temperature dependence of the magnetic susceptibility is given by the equation [18]:

$$\chi_M^{chain} = Ng^2\beta^2\{S_{Mn}(S_{Mn}+1)/3KT\}\{(1+\mu)/(1-\mu)\} \quad (1)$$

(Fisher's infinite chain model) with:

$$\mu = \coth[JS_{Mn}(S_{Mn}+1)/KT] - [KT/JS_{Mn}(S_{Mn}+1)] \quad (2)$$

The least-squares fit to the data leads to  $J = -0.084(3)$  cm<sup>-1</sup>,  $g = 1.99(5)$ ,  $R = 1.43 \times 10^{-5}$ . The small  $J$  value, which is comparable to the coupling values between the Mn(II) ions bridged by the diamagnetic cyanide precursors in other complexes,<sup>19</sup> suggests the overall very weak magnetic coupling between the Mn(II) ions with a long separation.

## Conclusion

In summary, three heterobimetallic cyanide-bridged Co(III)-Mn(II) one-dimensional single chain complexes have been rationally designed and successfully synthesized by purposefully using two *trans*-dicyanidecobalt(III) building blocks K[Co(L')(CN)<sub>2</sub>] and two seven-coordinated macrocyclic Mn(II) compounds, which are all favor of forming complexes with low dimensional structure. The magnetic studies demonstrate the weak antiferromagnetic interaction between the Mn(II) ions through [-NC-Co(L)-CN-] unit in the three Co<sup>III</sup>-Mn<sup>II</sup> cyanide-bridged complexes.

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