High-spin octahedral or pseudo-tetrahedral cobalt(II) complexes have been attracting much attention because they are potential candidates for single-ion magnets (SIMs). Although many SIMs with a first-row transition-metal have been reported, most of them do not exhibit a slow magnetic relaxation behavior in the absence of an external field due to fast relaxation via quantum tunneling. To prepare a zero-field SIM, not only a strong magnetic anisotropy, but also the molecular alignment of SIMs in the crystal, is important. Recently, zero-field SIM behavior in pseudo-tetrahedral cobalt(II) complexes with 2-(2-imidazolinyl)-6-methoxyphenolate (Hmimn–) was reported. It was suggested that hydrogen-bonded chain networks of [Co(Hmimn)₂] play a crucial role for slow magnetic relaxation in the absence of an external field. To elucidate the correlation between intermolecular magnetic coupling and quantum tunneling of magnetization, partial substitution of a paramagnetic ion by a diamagnetic ion in the crystal is an effective method. For such magnetic dilution experiments, it is important to prepare a diamagnetic analogue which is isomorphic to the SIM. In this study, an isomorphic Zn complex analogue of [Co(Hmimn)₂]·CH₃OH, [Zn(Hmimn)₂]·CH₃OH, was prepared and crystallographically characterized (Fig. 1).

The ligand precursor 2-(2-imidazolinyl)-6-methoxyphenol (H₂mimn) was synthesized according to a previously reported procedure. The title compound was obtained as colorless crystals from a reaction of ZnCl₂ (13.6 mg, 0.10 mmol), H₂mimn (38.4 mg, 0.20 mmol) and triethylamine (30 μL) in 10 mL methanol. Yield: 38.9 mg (81%).

The crystal structure of a pseudo-tetrahedral zinc(II) complex with a 2-(2-imidazolinyl)-6-methoxyphenolate ligand was determined by X-ray crystallography. The title compound was synthesized by a reaction of ZnCl₂ and 2-(2-imidazolinyl)-6-methoxyphenolate in methanol. The compound crystallizes in the monoclinic space group P2₁/c and Z = 4 with cell parameters a = 14.6485(5)Å, b = 19.2428(6)Å, c = 7.5851(3)Å, β = 104.253(4)°, V = 2072.26(13)Å³. The R₁ [I > 2σ(I)] and wR₂ (all data) values are 0.0304 and 0.0833, respectively, for all 4597 independent reflections. The title compound was found to take the bis-bidentate coordination mode. Intermolecular hydrogen-bonds were formed between the complexes to form a dimeric structure. Furthermore, hydrogen-bonds were formed between the dimer and a methanol molecule of crystallization to construct one-dimensional chain networks.

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Table 1 Crystal and experimental data

| Chemical formula: C₂₁H₂₆N₄O₅Zn | Formula weight = 479.83 |
| Crystal system: monoclinic | Space group: P2₁/c |
| a = 14.6485(5)Å | b = 19.2428(6)Å | c = 7.5851(3)Å |
| V = 2072.26(13)Å³ | Z = 4 |
| D₀ = 1.538 g/cm³ |
| Radiation: Mo Kα (λ = 0.71073 Å) |
| μ(Mo Kα) = 1.227 mm⁻¹ |
| Crystal size = 0.18 × 0.07 × 0.07 mm³ |
| No. of reflections collected = 14475 |
| No. of independent reflections = 4597 [R(int) = 0.0261] |
| θ range for data collection: 2.557 to 27.483° |
| Data/Restraints/Parameters = 4597/2/293 |
| Goodness-of-fit on F² = 1.063 |
| R indices [I > 2σ(I)]: R₁ = 0.0304, wR₂ = 0.0801 |
| R indices (all data): R₁ = 0.0402, wR₂ = 0.0833 |
| (Δρ)max = 0.002 |
| (Δρ)max = 0.489 eÅ⁻³ |
| Measurement: Rigaku XtaLAB AFC11 diffractometer |
| Program system: SHELXTL |
| Structure determination: intrinsic phasing methods (SHELXT-2018/2) |
| Refinement: full matrix least-squares (SHELXL-2018/1) |
| CCDC deposition number: 2049851 |

Fig. 1 Chemical structure of [Zn(Hmimn)₂]·CH₃OH.

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corrected with the ABSPACK scaling algorithm using CrysAlisPro. The initial structure was solved by an intrinsic phasing method with SHELXT-2018, and refined using a full-matrix least-squares method on $F^2$ utilizing SHELXL-2018. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the riding model, except for the N-H atoms, which are located by a difference Fourier map.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-2049851.

Table 2 Selected geometric parameters (Å, °)

| Distance | Angle |
|----------|-------|
| Zn1-O1   | 1.9388(13) |
| Zn1-O3   | 1.9312(13) |
| Zn1-N2   | 1.9464(15) |
| Zn1-N4   | 1.9563(15) |
| O1-Zn1-N2 | 95.17(6) |
| O1-Zn1-N4 | 911.88(6) |
| O3-Zn1-N2 | 109.33(6) |
| O3-Zn1-N4 | 94.60(5)  |
| O1-Zn1-O3 | 112.07(6) |
| N2-Zn1-N4 | 127.11(7) |

Symmetry codes (i) –x+2, –y+1, –z+1; (ii) –x+1, –y+1, –z+1.

Fig. 2 Molecular structure of [Zn(Hmimn)$_2$]·CH$_3$OH (50% probability level).

Fig. 3 One-dimensional chain structure along the a axis constructed by intermolecular hydrogen-bonding interactions in [Zn(Hmimn)$_2$]·CH$_3$OH. The intrachain Zn–Zn distance is shown (6.15 and 8.66 Å). The magenta and cyan lines indicate the intermolecular hydrogen-bonds.

In conclusion, a pseudo-tetrahedral zinc(II) complex [Zn(Hmimn)$_2$]·CH$_3$OH was successfully prepared and characterized. This crystal is isomorphous to a previously reported cobalt(II) analogue, which showed the SIM behavior in the absence of an external field. Since all of the structural parameters are nearly identical, a magnetic dilution experiment will shed light on the interesting zero-field single-ion magnetism.

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Supporting Information

A CIF format file. This material is available free of charge on the Web at http://www.jsac.or.jp/xraystruct/.

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