

STRUCTURE AND MAGNETISM OF A CHIRAL PEROVSKITE-LIKE DICYANAMIDOMETALLATE FRAMEWORK

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ABSTRACT. Perovskite-like compounds have attracted great attention because of their good properties, such as electrical, optical, and magnetic properties, etc. Herein, a new perovskite-like anionic dicyanamidometallate, namely (Bu₃MeP)[Ni(dca)₃] (**1**) (Bu₃MeP = tributylmethylphosphine cation, dca = dicyanamide), was synthesized and structurally characterized by elemental analysis, IR spectrum, thermogravimetric analysis, and single-crystal X-ray diffraction. The compound crystallizes in the tetragonal crystal system with the chiral space group *P*4₃2₁2, and exhibits a three-dimensional anionic dicyanamidometallate framework from Ni²⁺ units bridged by dicyanamides, in which tributylmethylphosphine cations are accommodated in the voids. The butyl groups present two conformations in the tributylmethylphosphine cation, resulting in chirality character occurred in compound **1**. Variable-temperature magnetic susceptibility analysis indicates that weak ferromagnetic interaction exists between the nickel(II) ions coupling by $\mu_{1,S}$ -bridging.

KEY WORDS: Perovskite-like, Dicyanamidometallate, Crystal structure, Magnetic properties

INTRODUCTION

Recently, perovskite-like compounds have recently attracted a lot of attention due to their amazing properties [1]. Particularly, molecular perovskites including coordination polymers or metal-organic frameworks were extensively studied during the last decade owing to their architectures regulated by vast diversity of guest molecules and different ligands [2]. Among the various of bridging ligands, dicyanamide (dca) plays an important role in building molecular perovskite-like compounds [3]. Thanks for the polar dicyanamide ligand, many interesting physical properties, such as the dielectric anomaly [4] and giant barocaloric effect [5], have been observed in the perovskites, originating from its conformational order/disorder transitions.

Besides, dca anion has been employed in constructing molecular magnetic materials due to its fantastic ability to convey magnetic interactions [6]. Comparing to the cyanide anion, the weak ligand field enable dca to stabilize the high spin states of metal ions [7], leading to magnetic order observed in some dicyanamidometallates [8]. In addition, dicyanamide anion can coordinate to a metal ion in a monodentate, bidentate, even as a tridentate manner, because of its two nitrile and one amido nitrogen atoms, and thus resulting in various structures [9]. Accordingly, a considerable number of perovskite-like dicyanamidometallates were investigated for their magnetic behaviours [10]. For instance, (Ph₄As)[Ni(dca)₃] shows long-range magnetic order with an ordering temperature of 20.1 K. Whilst, the compound of (Ph₃MeP)[Ni(dca)₃] does not present any order [11]. This phenomenon indicates that cation templating can be used to tune the magnetic behavior in the anionic dicyanamidometallates [12]. Tributylmethylphosphine cation, as one of templating, was rarely utilized to building perovskite-like dicyanamidometallates [13]. Hence,

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tributylmethylphosphine iodide, Ni(NO₃)₂ and sodium dicyanamide were chosen as the starting materials to assemble a perovskite-like compound, (Bu₃MeP)[Ni(dca)₃] (**1**). The compound shows chiral nickel-dicyanamide perovskite-like framework and weak ferromagnetic interactions.

EXPERIMENTAL

Materials and methods

All chemicals were of reagent grade and used as received from commercial sources (Shanghai Aladdin Biochemical Technology Co., Ltd) without further purification. Elemental analysis for carbon, hydrogen, and nitrogen was carried out with a Vario EL-III elemental analyzer. Infrared spectrum was recorded with a Nicolet A370 FT-IR spectrometer using KBr pellets in the 400–4000 cm⁻¹ region. TGA experiment was performed with a Mettler Toledo TGA/SDTA85e thermo gravimetric analyzer from 20 to 800 °C at a heating rate of 10 °C·min⁻¹ in air. Variable-temperature magnetic susceptibility measurement was taken at an applied field of 1 kOe on a Quantum Design MPMS-XL7 SQUID magnetometer working in 300–1.8 K temperature range. Diamagnetic correction was applied by using Pascal's constant.

Synthesis of (TriBuMeP)[Ni(dca)₃] (1)

A 1 mL of tributylmethylphosphine iodide (34.4 mg, 0.1 mmol) methanol solution was carefully layered onto 1 mL of Ni(NO₃)₂·6H₂O (29.0 mg, 0.1 mmol) water solution in a test tube (10 mL). Then, it was covered with 1 mL of sodium dicyanamide (26.8 mg, 0.3 mmol) methanol solution. After being static for a month, green single crystals were obtained (50%, respect to Ni), which is suitable for X-ray diffraction of **1**. Elemental analyses: calcd. for C₁₉H₃₀N₉PNi (%): C, 48.13; H, 6.38; N, 26.58. Found: C, 48.22; H, 6.56; N, 26.56. IR data (KBr, cm⁻¹): 3608(w), 2964(m), 2873(m), 2298(s), 2254(s), 2189(s), 1459(m), 1363(s), 927(m), 649(w), 505(m).

X-ray crystallography

The well-shaped single crystal of **1** was selected for X-ray diffraction study. Data collections were performed with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker Smart Apex-II CCD diffractometer, using the φ - ω scan technique. Data reduction was made with the Bruker SAINT package [14]. Absorption correction was performed using the SADABS program [15]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXTL-2018 program package [16]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated position. The absolute configuration was refined as an inversion twin. Crystallographic data and details on refinements are summarized in Table 1. Selected bond distances and angles are listed in Table 2.

RESULTS AND DISCUSSION

Crystal structure of 1

Single-crystal X-ray structural analysis reveals that compound **1** crystallizes in the tetragonal crystal system with the chiral space group $P4_32_12$. Compound **1** exhibits a similar perovskite-like architecture of the Mn-dca framework [13]. The atomic numbering asymmetric unit is illustrated in Figure 1, which contains one Ni²⁺ ion, one tributylmethylphosphine cation, and four independent $\mu_{1,5}$ -dca bridging ligands (two of them are half part). The central metal ion is coordinated by the six nitrile nitrogen atoms from dca ligands and represents an octahedral

coordination. The Ni–N bond lengths fall in the range of 2.055(6) to 2.073(6) Å (Table 2), comparing to those in (MV)[Ni₃(dca)₈] (MV²⁺ = methylviologen dication) [17].

Table 1. Crystallographic data and structure refinement for **1**.

Compound	1
Temperature (K)	296(2)
Formula	C ₁₉ H ₃₀ N ₉ PNi
Formula weight	474.20
Crystal system	Tetragonal
Space group	<i>P4₃2₁2</i>
<i>a</i> (Å)	11.66 2(5)
<i>b</i> (Å)	11.66 2(5)
<i>c</i> (Å)	33.90(3)
<i>α</i> (deg)	90
<i>β</i> (deg)	90
<i>γ</i> (deg)	90
<i>V</i> (Å ³)	4610(6)
<i>Z</i>	8
<i>D_c</i> (g cm ⁻³)	1.366
<i>μ</i> (mm ⁻¹)	0.936
<i>F</i> (000)	2000
<i>Flack</i>	0.50(6)
<i>R_{int}</i>	0.0437
GOF	1.090
<i>R</i> ₁ ^[a] , <i>wR</i> ₂ ^[b] [<i>I</i> > 2σ(<i>I</i>)] (<i>I</i>)	0.0487, 0.1206
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0634, 0.1323
[a] <i>R</i> ₁ = Σ <i>F</i> _o - <i>F</i> _c / Σ <i>F</i> _o	
[b] <i>wR</i> ₂ = [Σ <i>w</i> (<i>F</i> _o ² - <i>F</i> _c ²) ² / Σ <i>w</i> (<i>F</i> _o ²) ²] ^{1/2}	

Table 2. Selected bond lengths (Å) and angles [°] for compound **1**.

Compound 1					
Ni1—N1	2.059(6)	Ni1—N3	2.058(5)	Ni1—N5 ⁱ	2.055(6)
Ni1—N6	2.073(6)	Ni1—N8	2.061(5)	Ni1—N10 ⁱⁱ	2.073(5)
N1—Ni1—N6	178.1(2)	N1—Ni1—N8	90.7(2)	N1—Ni1—	90.1(2)
N3—Ni1—N1	90.0(3)	N3—Ni1—N6	91.7(3)	N3—Ni1—	179.7(3)
N3—Ni1—N8	90.9(2)	N5 ⁱ —Ni1—N1	89.4(2)	N5 ⁱ —Ni1—N3	89.9(2)
N5 ⁱ —Ni1—N6	91.5(2)	N5 ⁱ —Ni1—N8	179.2(2)	N5 ⁱ —Ni1—	89.8(2)
N6—Ni1—	88.3(3)	N8—Ni1—N6	88.3(2)	N8—Ni1—	89.4(2)

Symmetry codes: ⁱ x-1/2, -y+3/2, -z+1/4; ⁱⁱ x-1/2, -y+1/2, -z+1/4.

For its three nitrogen donor atoms, dicyanamide can present several possible coordination modes. Typically, its coordination mode is the bidentate form, which has been documented in abundant transition metals compounds [18]. In compound **1**, dicyanamide shows $\mu_{1,5}$ coordination mode. With the $\mu_{1,5}$ -mode dicyanamide bridges, each nickel ion is connected to the six nearest neighbor metal centers to form a porous cubic anionic framework [Ni(dca)₃]⁻ (Figure 2). While Bu₃MeP⁺ cations are embedded in the large crystal cavities and balance the negative charge of the framework (Figure 3). The Ni···Ni separations are 8.23 and 8.26 Å within the *ab*-plane, whereas 8.50 and 8.51 Å parallel to the *c*-axis. It is interesting that two conformations of butyl are observed in the tributylmethylphosphine cation (Figure 3), which is completely different from literature compounds [13, 19]. One butyl (C12-C15) shows skewed conformation with the torsion angle of 78°. Furthermore, the other two butyl groups emerge staggered conformation with torsion angles

of 171 and 169°, respectively. Thanks for the different conformations of butyl coexisting in one Bu_3MeP^+ cation, chirality arises in compound **1** [20].

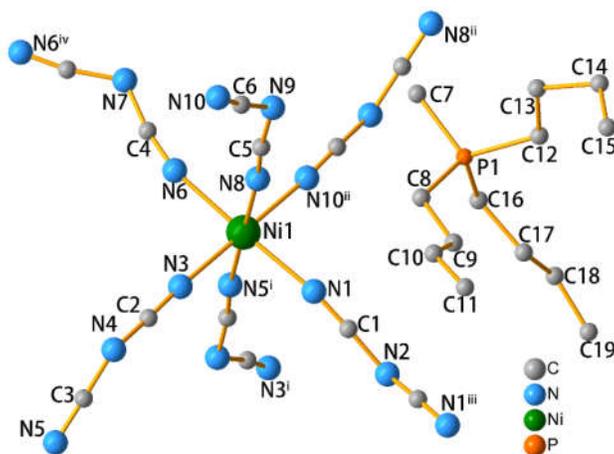
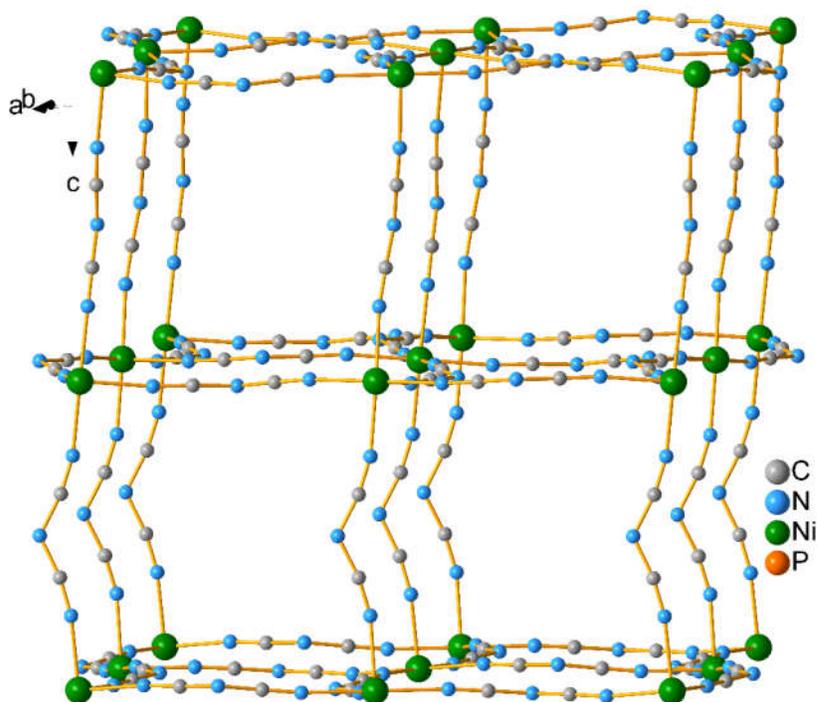


Figure 1. Molecular structure and coordination environment of compound **1**. Hydrogen atoms have been omitted for clarity; Symmetry codes: ⁱ $x-1/2, -y+3/2, -z+1/4$; ⁱⁱ $x-1/2, -y+1/2, -z+1/4$; ⁱⁱⁱ $-y+1, -x+1, -z+1/2$; ^{iv} $y, x, -z$.



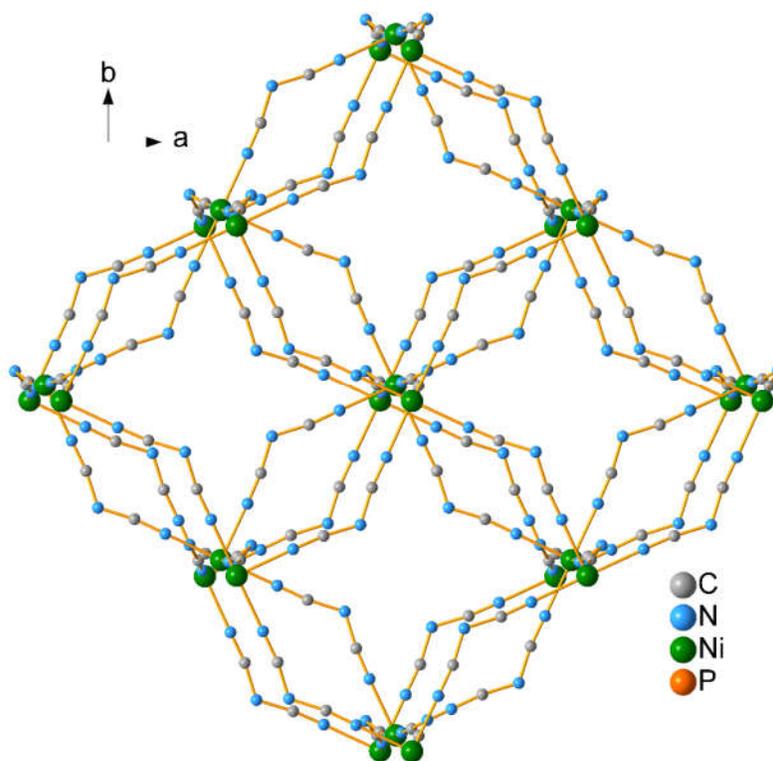


Figure 2. The anionic framework $[\text{Ni}(\text{dca})_3]^-$ along different directions. For clearly, Bu_3MeP^+ cations are deleted.

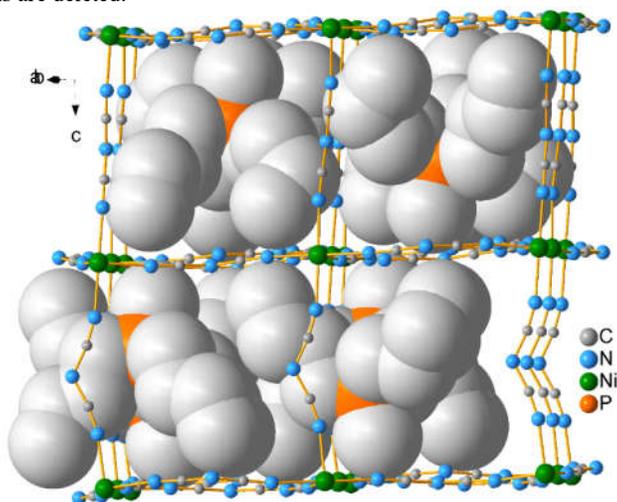


Figure 3. 3D framework of **1** showing the Bu_3MeP^+ cations (Space-Filling) embedded in the cavities.

IR spectrum

The IR spectrum of compound **1** (Figure 4) presents the characterization absorptions of dca with several strong absorption ν_{CN} bands at 2298(s), 2254(s), 2189(s) cm^{-1} , which can be assigned to $\nu_{\text{as+s}}$, ν_{as} , and ν_{s} vibrations, respectively [21]. The C-N symmetric stretch band (1363 cm^{-1}), the C-N asymmetric stretch band (927 cm^{-1}) can also be identified [22]. In compound **1**, the ν_{as} , and ν_{s} vibration bands are shifted to lower wave numbers. This phenomenon means that the charge density of dca ligands is high [23], indicating that $\mu_{1,5}$ -bidendate coordination mode occurred in **1**.

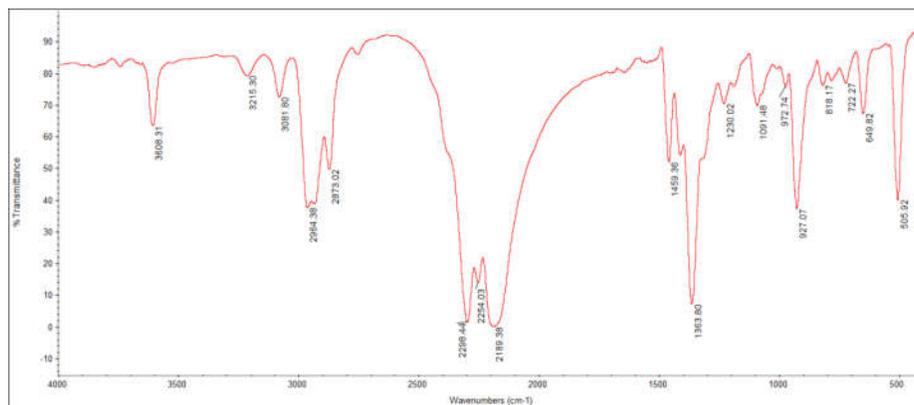


Figure 4. FT-IR spectrum of **1**.

Thermogravimetric analysis

Thermal stability of compound **1** was investigated in a heating rate of 10 K min^{-1} under an air atmosphere by TG technique and the thermogravimetric curve is shown in Figure 5. For compound **1**, the TGA plot indicates that the collapse of its skeleton comes up about 300 $^{\circ}\text{C}$, which is confirmed by the exothermic peak in DSC curve. Obviously, it can be found that only one endothermic peak occurs about 180 $^{\circ}\text{C}$ without any weight loss, which indicates phase transition processes [24].

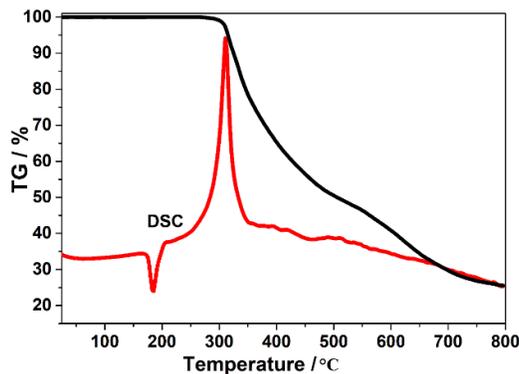


Figure 5. Thermogravimetric and DSC curves of compound **1**.

Magnetic properties

Magnetic susceptibility measurements of crystalline sample of **1** were carried out using a Quantum Design MPMS-XL7 SQUID magnetometer in an applied magnetic field of 1 KOe in the temperature range of 1.8–300 K. The results are shown in the form of $\chi_M T$ and χ_M^{-1} versus T (Figure 6). The $\chi_M T$ value of **1** is 1.35 emu K mol⁻¹ at room temperature, which is of the order expected spin-only value for one non-interacting nickel(II) ions [23, 25]. When the temperature is decreased, the $\chi_M T$ product remains almost constant in the range of 300–25 K, and then increases to a maximum value of 1.48 emu K mol⁻¹ at 16 K. Upon further cooling, the $\chi_M T$ plot decrease abruptly to a minimum value of 0.86 emu K mol⁻¹ at 1.8 K. This magnetic behavior is similar to that of compound TriBuMe[Ni(dca)₃] (TriBuMe = tributylmethylammonium) [10], indicating the presence of weak ferromagnetic interactions exist in **1** [26, 27]. In the whole temperature range, the magnetic susceptibility obeys the Curie–Weiss law with a Curie constant $C = 1.349(1)$ emu K mol⁻¹ and a positive Weiss constant $\theta = 0.5(1)$ K. The positive θ value furtherly suggests that there is weak ferromagnetic coupling in **1** [28, 29]. No peak can be observed in the χ_M -T curve (Figure 6), indicated no magnetic ordering occurred in **1** [30]. The field dependence of the magnetization of **1** also shows linear behavior at low fields, as expected for paramagnets [31]. Moreover, $M(H/T)$ shows clear tendency to saturation at higher fields and at 60 kOe achieves a value of about 2.36 N β , which is very close to the theoretical saturated moment of one Ni(II) ion [10].

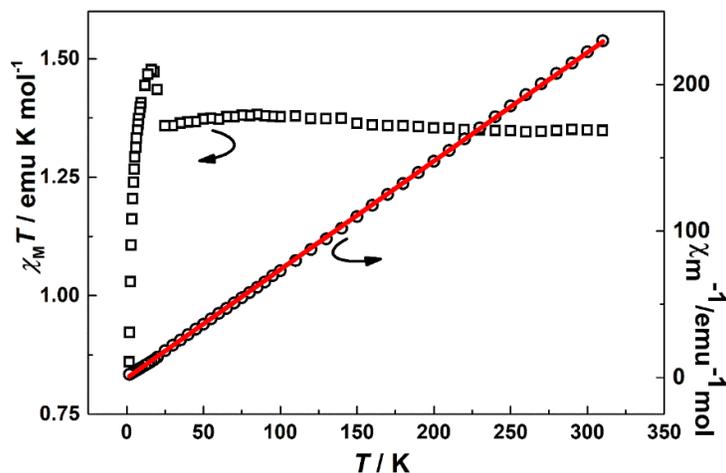


Figure 6. Plots of $\chi_M T$ and χ_M^{-1} vs T for **1**. Solid line represents the best fit of the data with Curie–Weiss law.

CONCLUSION

We have described the synthesis, single crystal structure and variable-temperature magnetic behavior of a new perovskite-like coordination polymer (Bu₃MeP)[Ni(dca)₃] (**1**). The compound appears a three-dimensional anionic framework from Ni²⁺ units bridged by dicyanamides, with tributylmethylphosphine cations embedded in the large crystal cavities. The chirality character of compound **1** maybe originate from two conformations of butyl coexisting in the tributylmethylphosphine cation. TG-DSC shows one endothermic peak observed without any weight loss, indicating phase transition processes in compound **1**. Variable-temperature magnetic

susceptibility analysis manifests that weak ferromagnetic interaction exists between the nickel(II) ions coupling by $\mu_{1,5}$ -bridgings.

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Supplementary material

Crystallographic data for structure **1**, described in this article has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 2300502, which can be obtained freely via E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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