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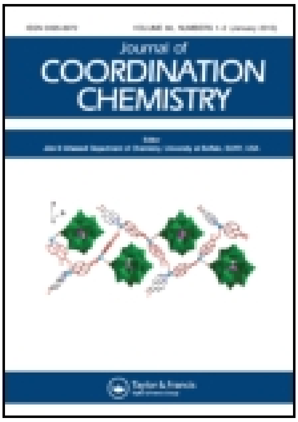

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A rare 4-connected neb topological framework based on Zn(II)

Fengxia Yue [a], Xiaoyang Yu [a c], Yuhui Luo [a], Jiajun Yang [a c], Xin Chen [b] & Hong Zhang [a]

[a] Department of Chemistry, Institute of Polyoxometalate Chemistry, Northeast Normal University, Changchun, P.R. China

[b] School of Pharmaceutical & Life Sciences, Changzhou University, Changzhou, P.R. China

[c] College of Chemical and Pharmaceutical Engineering, Jilin Institute of Chemical Technology, Jilin, P.R. China

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A rare 4-connected *neb* topological framework based on Zn(II)

FENGXIA YUE†, XIAOYANG YU†§, YUHUI LUO†, JIAJUN YANG†§, XIN CHEN*‡
and HONG ZHANG*†

†Department of Chemistry, Institute of Polyoxometalate Chemistry, Northeast Normal University, Changchun, P.R. China
‡School of Pharmaceutical & Life Sciences, Changzhou University, Changzhou, P.R. China
§College of Chemical and Pharmaceutical Engineering, Jilin Institute of Chemical Technology, Jilin, P.R. China

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A rare 4-connected *neb* framework, $[Zn(L)(bpmp)]_n$ (H_2L = 4,6-dibenzoylisophthalic acid; bpmp = *N*,*N′*-bis(4-pyridyl-methyl)piperazine), has been synthesized under hydrothermal conditions and characterized by powder X-ray diffraction, IR, elemental analysis, and single crystal X-ray diffraction. The complex exhibits a rare threefold interpenetrating *neb* framework and displays double right- and left-handed helical chains. The luminescence property of the complex has also been studied.

Keywords: Topology; Interpenetration; Crystal structure; Hydrothermal reaction; Luminescence

1. Introduction

Coordination polymers have promising potential applications [1–4]. As an important class, topological networking attracts much attention due to its helpfulness for structure analyses and as a guiding role for rational design and synthesis of functional materials [5–9]. With the development of coordination polymers, a variety of network topologies have been discovered, such as three-, four-, six-, eight- and even higher-connecting networks [10]. The nodes of 4-connected networks are common in crystal chemistry, such as diamond, NbO, PtS, etc. [11–13]. Among the 4-connected networks, the diamond network has been the most reported. Discovery of 4-connected networks is an important field in topology [14–16]. Helical structures are ubiquitous in nature and are the foundation of the genetic code, attracting interest in coordination chemistry, and material chemistry owing to their importance in biological systems, asymmetric catalysis, and optical devices. Here, we report the synthesis of such an unusual 4-connected helical framework.

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*Corresponding authors. Email: xinchen@cczu.edu.cn (X.Chen); zhangh@nenu.edu.cn (H.Zhang)

Compared to other dicarboxylate coordination polymers [17–24] summarized in our previous work [25–27], 4,6-dibenzoylisophthalic acid (H_2L) is an excellent ligand in the assembly of coordination polymers. H_2L can slightly change the dihedral angle of benzoyl to meet the requirements of coordination [28] and the benzoyl can form $C/O–H\cdots O$, $C/O–H\cdots\pi$, and $\pi\cdots\pi$ interactions as steering forces on the control of molecular self-assembly. Here, we choose H_2L and *N*,*N*′-bis(4-pyridyl-methyl)piperazine (bpmp) to control the structure and dimensionality of the resulting coordination polymer. We synthesized [Zn(L)(bpmp)], which exhibits a rare threefold interpenetrating *neb* network with the helical structure. Additionally, the luminescence property of the complex is studied.

2. Experimental

2.1. *Materials and instrumentation*

Chemicals were purchased from commercial sources and used without purification. H_2L and bpmp were synthesized according to the literature method [29, 30]. FT-IR spectra were measured in KBr pellets from 4000 to 400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analysis for C, H, and N was performed on a Perkin–Elmer 2400 Elemental Analyzer. Thermogravimetric analysis was performed on a Perkin–Elmer Thermal Analyzer under nitrogen at a heating rate of 5 °C min^{-1}. Luminescence studies were performed on a FLS920 Edinburgh Luminescence Spectrometer.

2.2. *Synthesis of [Zn(L)(bpmp)]*

A mixture of $ZnCl_2$ (13.6 mg, 0.1 mM), H_2L (37.4 mg, 0.1 mM), bpmp (26.8 mg, 0.1 mM), and H_2O (10 mL) was stirred for 30 min and the pH of the solution was adjusted to 5.5 with 0.1 M NaOH solution. Then, it was sealed in a 25 mL Teflon reactor and heated at 160 °C for 72 h. Next, the reaction system was cooled to room temperature at 3 °C h^{-1} to generate colorless prismatic crystals (49% yield based on Zn(II)). Anal. Calcd for $C_{38}H_{32}ZnN_4O_6$ (706.05): C, 64.64; H, 3.14; N, 7.94%. Found: C, 64.80; H, 3.20; N, 7.87%. IR (KBr, cm^{-1}): 3068 (*w*), 2954 (*w*), 2830 (*w*), 1668 (*s*), 1621 (*s*), 1430 (*m*), 1343 (*s*), 1253 (*m*), 1170 (*w*), 1134 (*w*), 1016 (*w*), 908 (*w*), 805 (*m*), 707 (*m*), 620 (*w*), 579 (*w*), 491 (*w*).

2.3. *X-ray crystallography*

Single crystals were glued to fiberglass for data collection on a Rigaku Mercury CCD diffractometer equipped with Mo–*K*α radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS. The structure was solved by direct methods by the difference Fourier method and refined by full-matrix least-squares on F^2 using the SHELXS-97 package. All non-hydrogen atoms were refined anisotropically and hydrogens of ligands are located by Fourier maps, and then refined by riding mode. The detailed crystallographic data and structure refinement parameters are summarized in table 1. Selected bond lengths and angles are listed in table 2.

Table 1. Crystal data and structure refinement for the complex.[a,b]

Formula	$C_{38}H_{32}ZnN_4O_6$
Formula weight	706.05
Crystal system	Monoclinic
Space group	*C2/c*
a/Å	18.451(6)
b/Å	16.466(5)
c/Å	23.079(7)
α/°	90
β/°	102.669(6)
γ/°	90
V/Å^3	6841(4)
Z	8
D_c/g cm^{-3}	1.371
μ/mm^{-1}	0.771
F (000)	2928
2θ range/°	2.02–25.10
Reflns. collected/unique	21,958/5980
R_{int}	0.0763
Goodness of fit on F^2	1.117
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0641, 0.1632
R_1, wR_2[b] (all data)	0.1001, 0.1954

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$; [b] $wR_2 = \sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]^{1/2}$.

Table 2. Bond lengths [Å] and angles [°] for the complex.[a]

Zn(1)–O(1)	1.938(3)	Zn(1)–N(3)	2.014(4)
Zn(1)–O(3)	1.948(3)	Zn(1)–N(1)	2.036(5)
O(1)–Zn(1)–O(3)	98.97(14)	O(1)–Zn(1)–N(1)	107.98(17)
O(1)–Zn(1)–N(3)	110.55(15)	O(3)–Zn(1)–N(1)	106.55(16)
O(3)–Zn(1)–N(3)	116.83(17)	N(3)–Zn(1)–N(1)	114.58(18)

[a] Symmetry code: #1 $1-x$, $1-y$, $-z$.

3. Results and discussion

3.1. *Description of the structure*

Single crystal X-ray diffraction analysis reveals that the complex crystallizes in the monoclinic space group *C2/c*. The asymmetric unit comprises one crystallographically independent Zn(II), one L anion, and two halves of bpmp. As shown in figure 1, Zn1 is coordinated by O1 and O3 from two L (Zn–O 1.938(3) and 1.948(3) Å) and N1 and N3 from two bpmp (Zn–N 2.014(4) and 2.036(5) Å), forming a distorted ZnN_2O_2 tetrahedron. In the complex, the μ_2–$\eta^1:\eta^0:\eta^1:\eta^0$-bridging L linkers adopting bis-monodentate coordination connect Zn(II) sites into a zigzag chain along the *b*-axis (figure 2(a)). For L^{2-}, two benzoyl groups locate on the same side of the central benzene ring with torsion angle of C3–C8–C9–C10 of −66.22(6)° and C5–C6–C16–C17 of 86.97(5)° (figure S1). Then each chain is connected by four neighboring chains through bpmp to form a 3-D architecture (figure 2(b)). Inspection of the structure confirms double right- and left-handed helical chains of $[Zn–bpmp–Zn–bpmp–Zn–L–]_n$ running along the *b*-axis with pitch of 32.932 (10) Å, as shown in figure 2(c). From the topological view, each Zn(II) connecting two L and two bpmp can be simplified as a 4-connected node, thus the framework is described as a 4-connected *neb* network with the long Schläfli vertex symbol [31] of $6 \cdot 6 \cdot 6 \cdot 6_2 \cdot 6_2 \cdot 6_2$

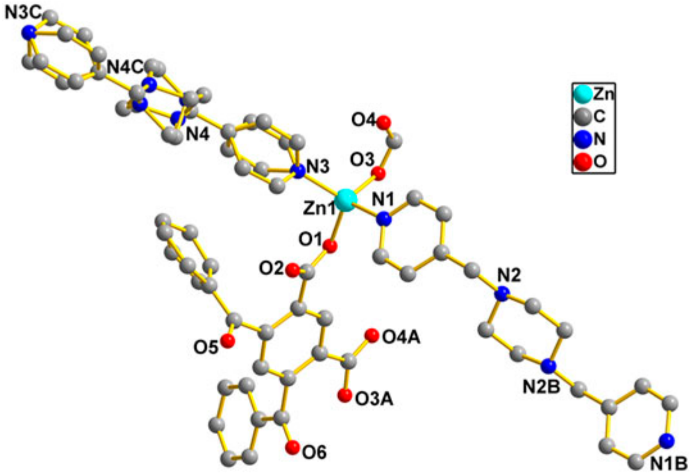

Figure 1. Coordination environment of Zn(II) (symmetry codes: A, $-x+1/2$, $y+1/2$, $-z+1/2$; B, $-x$, $-y+1$, $-z+1$; C, $-x+3/2$, $-y+1/2$, $-z+1$). All hydrogens are omitted for clarity.

(figure 3(a)). In the *neb* network, the nodes are connected into four chair-like six-membered rings and two distorted boat-like six-membered rings (figure 3(b)) to form a very unusual 6^6 cage named "isodiamantane" by Ermer and Eling [32]. This 3-D framework possesses three-directional open windows of 16.2×19.6 Å^2 along the [0,1,0] direction, of 16.5×16.2 Å^2 along the [17,0,10] direction, and of 16.5×16.5 Å^2 along the [7,0,−10] direction. However, the large void spaces are minimized because of the presence of threefold interpenetration (figure 3(c)). Significant intramolecular C–H···O interactions (H(23)···O(2), 2.459 Å; C(23)···O(2), 3.266(7) Å, 146°) and internetwork C–H···π (table 3) interactions help to stabilize the structure (figure 4).

3.2. *IR spectroscopy*

In the FT-IR spectrum of the complex (figure S2), the band at 3068 cm^{-1} can be attributed to C–H stretching vibration of the aromatic ring. Bands at 2954 and 2830 cm^{-1} are $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ stretches of bpmp. The band at 1621 cm^{-1} belongs to $\nu_{as}(COO^-)$ of carboxylate and a strong band at 1343 cm^{-1} corresponds to $\nu_s(COO^-)$ of carboxylate. Compared to the spectrum of H_2L, the strong band at 1668 cm^{-1} could be attributed to the stretch of carbonyl.

3.3. *PXRD analysis*

The products have been characterized by powder X-ray diffraction (PXRD) (figure S3). The experimental PXRD patterns corresponded well with the results simulated from the single crystal data, indicating high purity of the synthesized samples. The differences in intensity may be due to the preferred orientation of the powder samples.

3.4. *Luminescence*

The solid-state emission and excitation spectra of the complex, free H_2L, and bpmp at room temperature are depicted (figure 5(a) and S4). The luminescence spectra of H_2L and

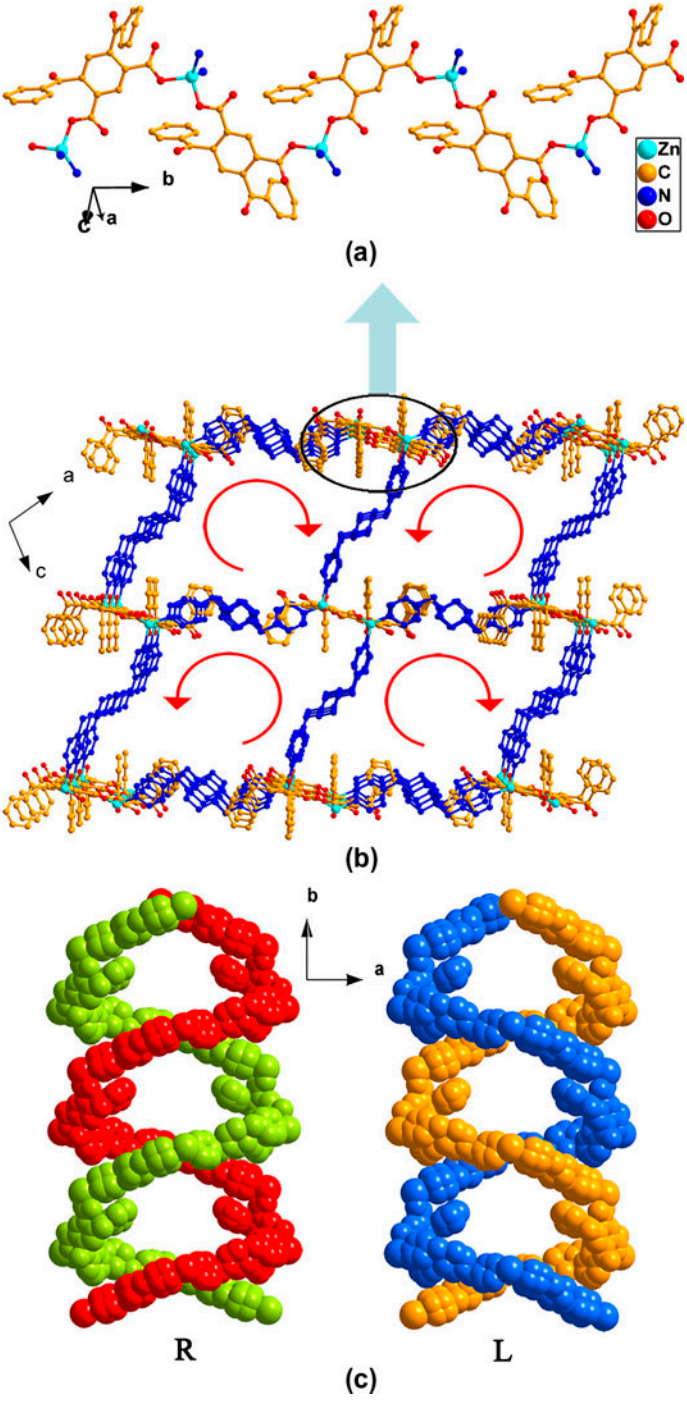

Figure 2. (a) View the 1-D zigzag chain along the *b*-axis. (b) 3-D architecture constructed by bpmp (blue atoms) and alternate arrangement of right- and left-handed helical channels. (c) Space-filling representation of double right- and left-handed helical chains along the *b*-axis. All hydrogens are omitted for clarity (see http://dx.doi.org/10.1080/00958972.2013.816691 for color version).

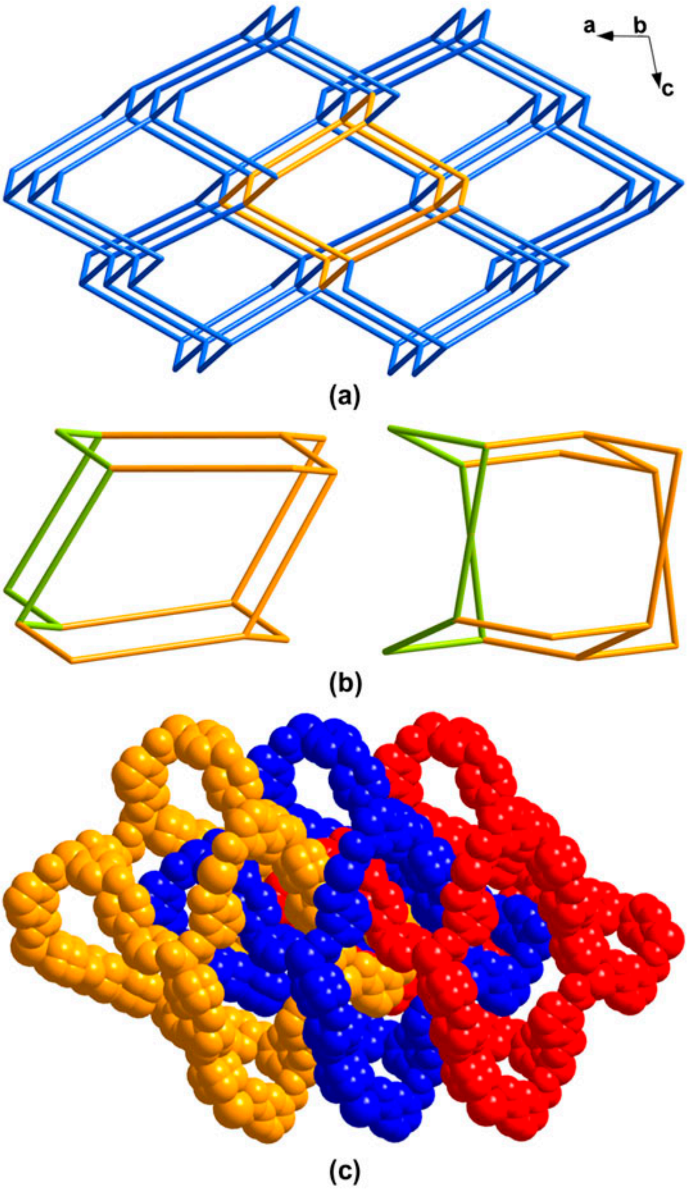

Figure 3. (a) A schematic view of the *neb* network with a 6^6 cage unit (highlighted in yellow). (b) The chair-like six-membered rings and the distorted boat-like six-membered rings (highlighted in green) in the basic unit of *neb* topology. (c) Space-filling representation of threefold interpenetrating isodiamantanoid cages. All hydrogens and benzoyl groups are omitted for clarity (see http://dx.doi.org/10.1080/00958972.2013.816691 for color version).

bpmp display the emission peak at 454 ($\lambda_{ex} = 373$ nm) and 528 nm ($\lambda_{ex} = 310$ nm), respectively. The emission can be attributed to $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions as previously reported [33, 34]. The emission spectra of the complex exhibit a broad emission maximum at 470 nm ($\lambda_{ex} = 380$ nm). Since Zn(II) ions are difficult to oxidize or reduce, the emission is neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer [35, 36].

Table 3. C–H···π interactions in the complex.[a]

C–H···π	Symmetry code	H–C(g) (Å)	X–H···C(g) (°)	X···C(g) (Å)
C(38)–H(38B)>Cg(6)	$x-1/2$, $y+1/2$, z	2.87	127	3.534(7)
C(38′)–H(38C)>Cg(6)	$x-1/2$, $y+1/2$, z	2.85	133	3.589(12)

[a] Cg(6): C(3) > C(4) > C(5) > C(6) > C(7) > C(8).

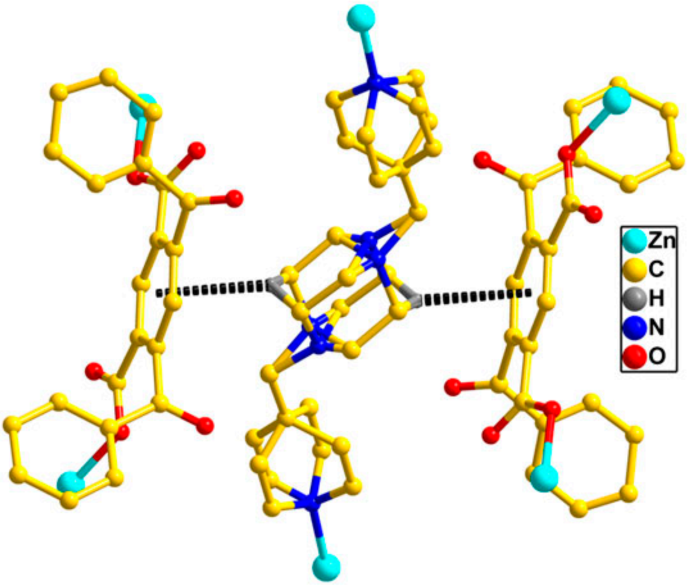

Figure 4. Inter-network C–H···π interactions. Remaining hydrogens are omitted for clarity.

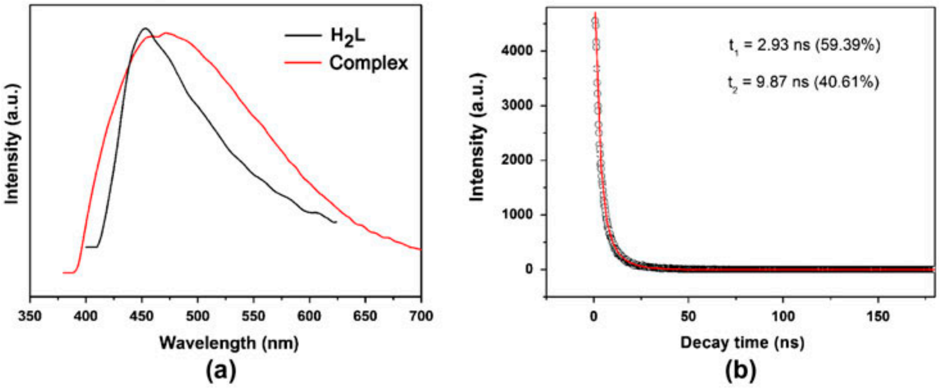

Figure 5. (a) Solid-state emission spectra of the complex and free H_2L and bpmp at room temperature. (b) Luminescence decay curve for the complex.

Emission peaks of the complex are near to that of free H_2L, so the emissions of the complex can be attributed to the intraligand fluorescent emissions [37, 38]. Compared with the emission spectrum of H_2L, red shift of the emission bands for the complex are observed, due to deprotonation and coordination to Zn(II) [35, 39]. The luminescence decay curve of the complex can be best fitted with a double exponential decay function with $\tau_1 = 2.93$ ns (59.39%) and $\tau_2 = 9.87$ ns (40.61%) ($\chi^2 = 1.089$, figure 5(b)).

4. Conclusion

We have prepared and characterized a rare threefold interpenetrating *neb* topological network with double right- and left-handed helical chains. The 3-D framework possesses three-directional open windows. However, the large void spaces are minimized by threefold interpenetration. Significant intramolecular C–H···O and internetwork C–H···π interactions help to stabilize the structure. This work provides helpful information for design and construction of rare topological networks. Luminescence reveals that the complex has applications in optical and electrooptical devices as well as time-resolved luminescence assays.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center; CCDC number is 890981 for the title complex. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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