

Electronic Supplementary Information (ESI)

Coexistence of a pair of enantiomorphic forms of the chiral quartz nets with a interpenetrating mode in a centrosymmetric coordination polymer

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Experimental Section

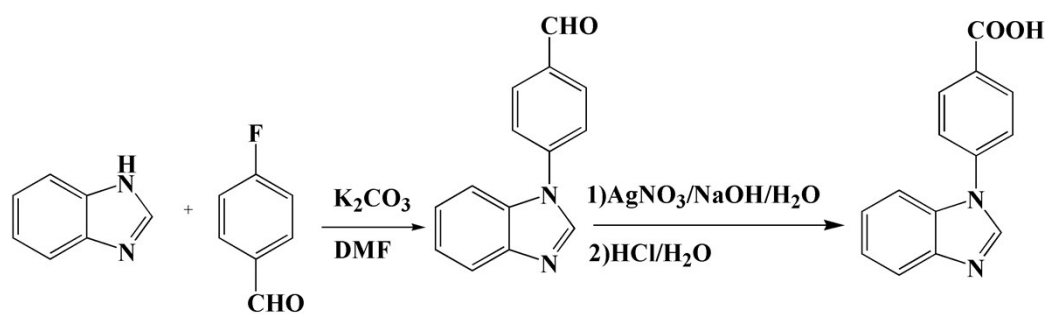
General. All chemicals were of reagent grade and used as commercially obtained from Sinopharm Chemical Reagent Co., Ltd, China.

NMR spectrum, Elemental Analysis, and Infrared Spectroscopy. NMR analyses were conducted on a Bruker Avance 400 spectrometer equipped with an automatic sample holder. Chemical shift data for each signal are reported in ppm units with DMSO as reference, where δ (DMSO) = 2.50 ppm. Elemental analyses were carried out on an Elementar Vario EL III analyzer and IR spectra (KBr pellets) were recorded on PerkinElmer Spectrum One.

Thermogravimetric analysis. The thermogravimetric measurements were performed with a Netzsch STA449C apparatus under a nitrogen atmosphere with a heating rate of 10 °C/min in the Al₂O₃ containers.

Powder X-ray Diffraction. Powder X-ray diffraction patterns were performed on a Rigaku Miniflex II powder diffractometer using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. The 2θ range was 5–60° with a continuous scan step width of 0.05°. The recorded patterns were compared with theoretical patterns calculated from single-crystal structure data. The simulated powder patterns were calculated using

Mercury 2.3 program.



Scheme S1. Preparation of Hbmzbc ligand.

Synthesis of Htzbc ligand (Scheme 1).

The Hbmzbc ligand was prepared following a modified known procedure.¹ 0.1 ml tetrabutylammonium chloride was added dropwise to a 10 mL of DMF containing a mixture of 1H-benzimidazole (3.894 g 0.033 mol) and potassium carbonate (4.6 g 0.033 mol) in 50 mL three-neck flask under stirring. The reaction mixture was heated at 90 °C for 10 minutes. Then 4-fluorobenzaldehyde (2.302 g, 0.033 mol) was gradually added to a stirred solution of the reaction mixture. The resulted mixture was vigorously stirred at 90 °C for 24 h to form a yellow precipitate. After cooling to room temperature, 50 mL ice water was added to the reaction mixture. The resulting yellow precipitate was collected by filtration, and washed with Et_2O (5 mL). The product dried at 60 °C to afford the intermediate, 4-(benzimidazole-1-yl)benzaldehyde. 4-(Benzimidazole-1-yl)benzaldehyde (2.22 g 0.01 mol) and $AgNO_3$ (3.4 g, 0.02 mol) were added to a 60 mL 7% NaOH solution in 100 mL flask. The reaction mixture was slowly heated to 60 °C and stirred for 24 h at this temperature. After cooling to room temperature, the insoluble material was removed by filtration and then rinsed with H_2O (20 mL). The filtrate was acidified ($pH \approx 2$) by addition of concentrated 1 mol/L⁻¹ HCl to form a pink precipitate. The pink precipitate was collected by filtration and washed with Et_2O (5 mL). The crude product was recrystallized from hot ethanol to yield the Hbmzbc ligand as colorless crystals. Yield 1.91 g (80.2 %). ¹H-NMR (400 MHz, $DMSO-d_6$, δ , ppm): 8.93 (s, 1H), 8.18 (d, 2H),

7.88 (d, 2H), 7.86-7.71 (m, 2H), 7.43 (m, 2H). Anal. calcd. for C₇H₅NO (119.12): C, 70.58; H, 4.23; N, 11.76%. Found: C, 70.62; H, 4.21; N, 11.72%. IR spectrum(cm⁻¹, KBr pellet): 3443 (s), 3074 (m), 2647 (w), 2426 (w), 1957 (w), 1719 (s), 1643 (w), 1607 (s), 1582 (w), 1520 (m), 1499 (w), 1479 (m), 1429 (m), 1384 (s), 1323 (w), 1234 (m), 1177 (w), 1120 (m), 1013 (w), 868 (w), 801 (m), 692 (w), 742 (s), 695 (m), 614 (w), 579 (w), 525 (w), 480 (w).

Synthesis of {[Zn₃(bzmzbc)₆]·11.5(DMF)}_n (1). A mixture of Zn(NO₃)₂·6H₂O (0.0298 g, 0.1 mmol), 4-(benzimidazole-1-yl)benzoic acid (0.0714 g, 0.3 mmol) and methanamine (0.05 mL) in 10 mL DMF was sealed in a 25 mL Parr Teflon-lined stainless steel vessel. The vessel was sealed and heated to 120 °C. This temperature was kept for 3 days and then the mixture was cooled naturally to form the resulting pale brown solution. Pale yellow crystals of **1** were obtained upon evaporation of the resulting solution for one week (yield: 0.0247g, 83% on the basis of Zn). Anal. calcd. for C₈₄H₅₄N₁₂O₁₂Zn₃ (1619.50): C, 62.30; H, 3.36; N, 10.38%. Found: C, 59.60; H, 4.86; N, 12.31%. Main IR features (cm⁻¹, KBr pellet): 3430 (s), 3096 (w), 1666 (s), 1605 (m), 1566 (m), 1516 (s), 1498 (w), 1480 (w), 1461 (s), 1382 (s), 1323 (m), 1300 (m), 1238 (s), 1175 (m), 1137 (w), 1100 (m), 1062 (w), 1012 (m), 993 (s), 937 (w), 913 (m), 867 (m), 846 (w), 790 (s), 777 (w), 763 (w), 746 (s), 702 (m), 654 (w), 620 (w), 582 (w), 532 (w), 490 (m), 427 (w).

Elemental analyses for **1** showed that the observed values are much different from those of calculated. This because the observed values from the sample of **1** contain the disordered solvents, which are not modeled from the X-ray single-crystal diffraction data.

The amount of the guest DMF molecules per formula unit is established by the amount of electron density that is removed from the crystal structure via SQUEEZE program and thermogravimetric analyses.

X-ray Crystallography. Single crystal X-ray diffraction data of Hbmzbc compound and compound **1** were collected on a Bruker Apex II CCD diffractometer equipped with a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Data reduction was performed using SAINT and corrected for Lorentz and polarization effects.

Adsorption corrections were applied using the SADABS routine.² The structures were solved by the direct methods and successive Fourier difference syntheses, and refined by the full-matrix least-squares method on F^2 (SHELXTL Version 5.1).³ All non-hydrogen atoms are refined with anisotropic thermal parameters. Hydrogen atoms were assigned to calculated positions. The DMF solvents in **1** were highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these residual solvents were removed from the data using the SQUEEZE routine of PLATON⁴ and refined further using the data generated. One of the benzimidazole rings was disordered over two positions. The SIMU, ISOR and DELU restraints have been used in the refinements due to the large thermal displacement parameters for some C and O atoms. The R_1 values are defined as $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$. The details of the crystal parameters, data collection, and refinement are summarized in Table 1.

Table S1. Crystallographic Data for Compound **1**^a.

	Hbmzbc	1
formula	C ₇ H ₅ NO	C ₈₄ H ₅₄ N ₁₂ O ₁₂ Zn ₃
fw	119.12	1619.50
temp (K)	296(2)	296(2)
cryst syst	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
Z	16	4
a (Å)	11.0915(2)	36.070(2)
b (Å)	13.6907(4)	21.1700(12)
c (Å)	15.0334(4)	17.8547(11)
α (deg)	90	90
β (deg)	91.931(2)	91.220(4)
γ (deg)	90	90

V (Å ³)	2281.53(10)	13630.6(14)
D_{calcd} (g·cm ⁻³)	1.387	0.789
μ (mm ⁻¹)	0.095	0.564
no. of reflns collected	21084	54258
independent reflns	5234	15704
obsd reflns. ($I > 2\sigma(I)$)	3229	6724
$F(000)$	992	3312
R [int]	0.0476	0.0529
R_1 ($I > 2\sigma(I)$)	0.0469	0.0715
wR_2 (all data)	0.1276	0.2226

^a $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

Table S2. Selected bond distances for Compound **1**^a.

Zn(1)–O(1)	1.938(3)	Zn(1)–O(5)	1.958(3)
Zn(1)–N(6A)	2.008(3)	Zn(1)–N(4)	2.024(3)
Zn(2)–N(2B)	2.010(3)	Zn(2)–N(2)	2.010(3)
Zn(2)–O(4C)	2.028(4)	Zn(2)–O(4D)	2.029(4)

Symmetric codes: A $-x + 1/2, y + 1/2, -z + 3/2$; B $-x + 1, y, -z + 1/2$; C $x + 1/2, y + 1/2, z$; D $-x + 1/2, y + 1/2, -z + 1/2$.

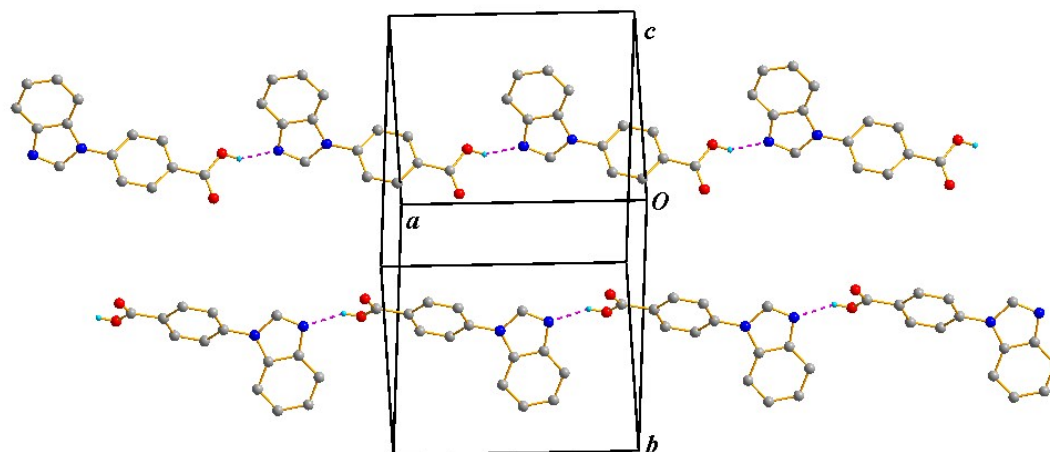


Figure S1 There are two crystallographically independent Hbmzbc molecules in the asymmetric unit of the organic compound. The hydrogen bonds ($O \cdots N = 2.655(2)$ and $2.649(2)$ Å) between the carboxylic groups and benzimidazole N atoms link the Hbmzbc molecules to give a 1D chains running along *a* direction.

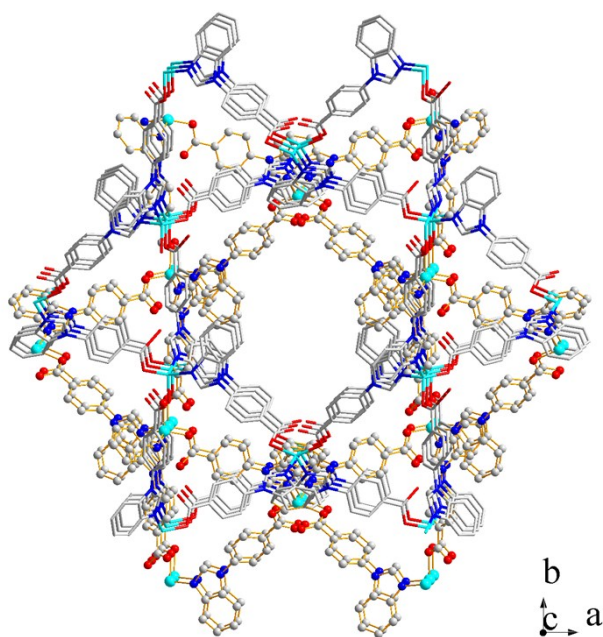


Figure S2 The two interpenetrating networks in **1** discriminated by ball and wire modes, respectively.

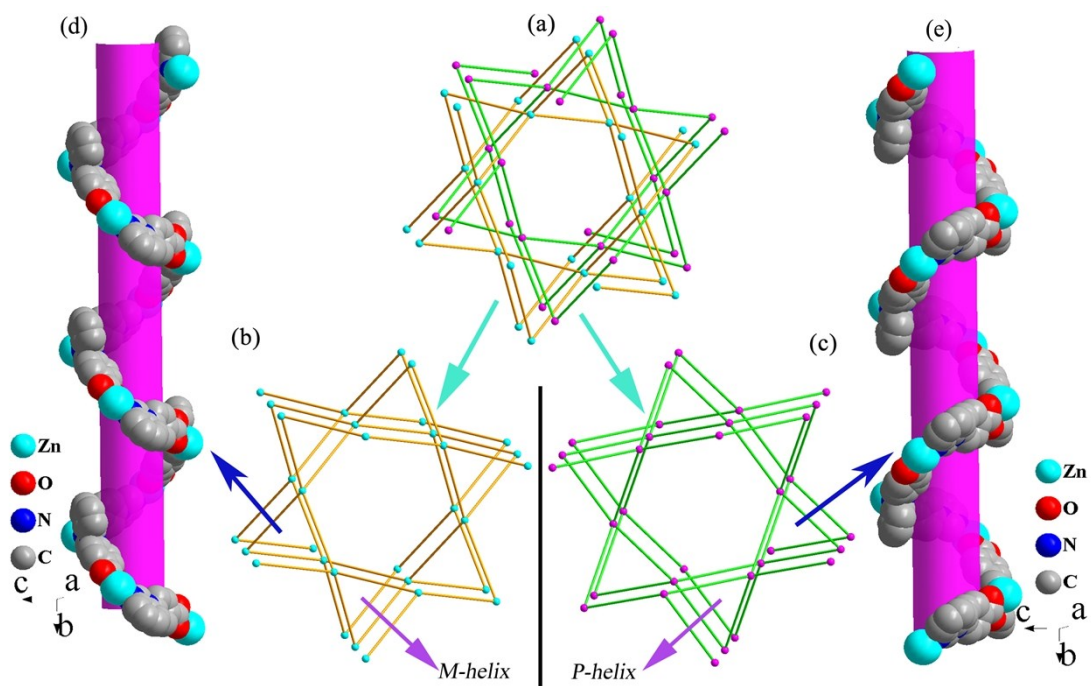


Figure S3 (a) The 2-folded interpenetrating **qtz** network of **1** discriminated by colors; (b) a single **qtz** net with *M*-configuration and (c) with *P*-configuration in **1**; (d) the left-handed helical chain in one **qtz** net and the right-handed helical chain in its interpenetrating **qtz** net.

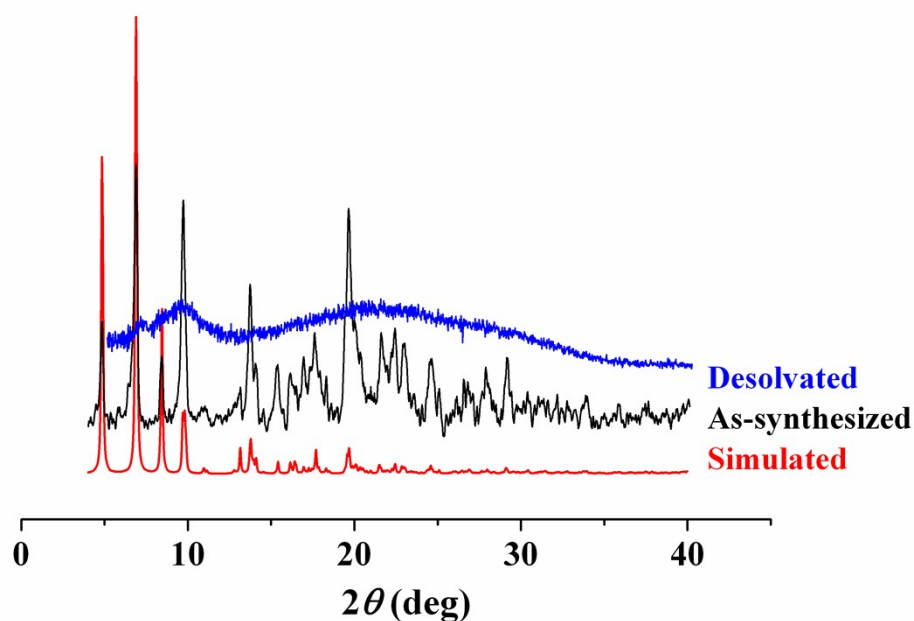


Figure S4 Powder X-ray diffraction patterns for **1**. Few small extra peaks in the PXRD pattern of the as-synthesized at the low angle should belong to the contribution from the disordered solvent molecules that have been removed by SQUEEZE during structure determination.

Luminescent properties

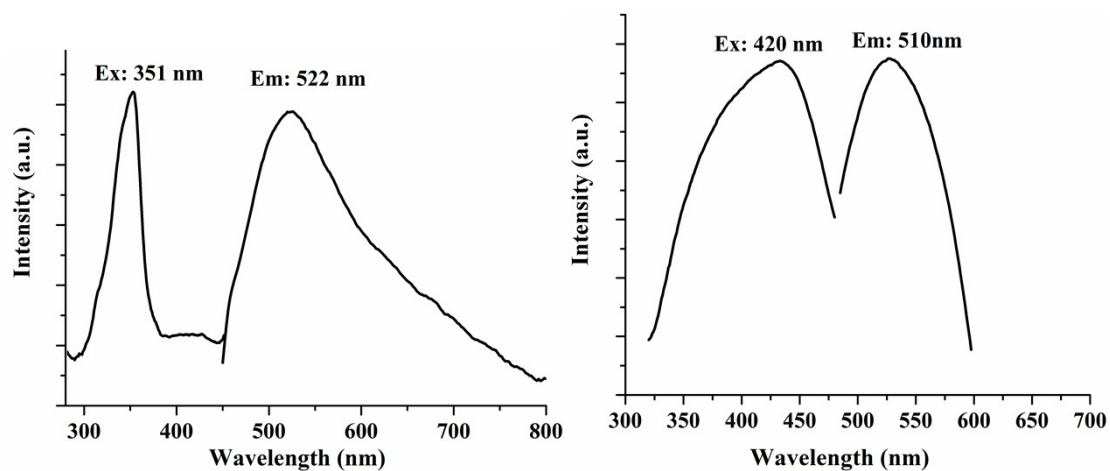


Figure S5 The solid-state photoluminescent spectra of Hbmzbc ligand ($\lambda_{\text{ex}}=351\text{ nm}$) (left) and compound **1** ($\lambda_{\text{ex}}=430\text{ nm}$) (right) at room temperature.

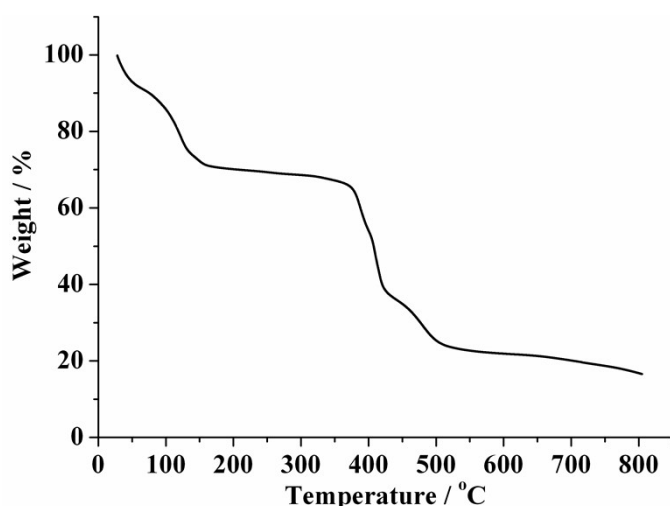


Figure S6 TGA curve for **1**.

2-fold **qtz** nets:

There are forty-one structures with the 2-fold **qtz** topological nets have been reported. Table S3 lists the detailed CCDC Refcode in the Cambridge Crystallographic Data Centre and references for these structures.

Table S3. The CCDC Refcode and the references related the structures of the reported 2-fold **qtz** nets.

<i>Refcode in CCDC</i>	<i>Space group</i>	<i>Reference</i>
BERQAS	$P6_222$	<i>CrystEngComm</i> . 2013, 15, 3470
BERQEW	$P6_222$	<i>CrystEngComm</i> . 2013, 15, 3470
CEKROB	$P3_221$	<i>CrystEngComm</i> . 2012, 14, 7320
CEKRUH	$P3_2$	<i>CrystEngComm</i> . 2012, 14, 7320
CUWPUG	$P2_1212$	<i>Cryst. Growth Des.</i> 2010, 10, 1307
CUWQAN	$P2_1212$	<i>Cryst. Growth Des.</i> 2010, 10, 1307
FOMYAI	$P6_4$	<i>Acta Crystallogr. Sect. E:Struct. Eep. Online.</i> 2005, 61, m1075
GAGWOB	$P2_12121$	<i>Dalton Trans.</i> 2004, 21, 3440
GAGWUH	$P3_221$	<i>Dalton Trans.</i> 2004, 21, 3440
GAGWUH01/ GAGWUH02	$P3_121$	<i>Inorg. Chem. Commun.</i> 2011, 14, 411 <i>J. Coord. Chem.</i> 2013, 66, 926
HAGPUA	$P6_2$	<i>Acta Chem. Scand.</i> 1993, 47, 728
LARVIL	$P6_222$	<i>Inorg. Chim. Acta.</i> 2012, 384, 287

LAZJAZ	$P2$	<i>Cryst. Growth Des.</i> 2012, 12, 3426
PAPNUR	$P3_221$	<i>Cryst. Growth Des.</i> 2011, 11, 5592
PAPPAZ	$P3_221$	<i>Cryst. Growth Des.</i> 2011, 11, 5592
PAPPED	$P3_221$	<i>Cryst. Growth Des.</i> 2011, 11, 5592
PAPPIH	$P3_221$	<i>Cryst. Growth Des.</i> 2011, 11, 5592
PASGEX	$P3_121$	<i>CrystEngComm.</i> 2012, 14, 4165
PASGEX01/ PASGEX02 PASGEX03/ PASGEX04	$P3_121$	<i>CrystEngComm.</i> 2012, 14, 4165
PASGIB	$P3_221$	<i>CrystEngComm.</i> 2012, 14, 4165
PASGIB01/ PASGIB02 PASGIB03/ PASGIB04	$P3_221$	<i>CrystEngComm.</i> 2012, 14, 4165 <i>Cryst. Growth Des.</i> 2012, 12, 3917
PELRAB	$P3_221$	<i>CrystEngComm.</i> 2013, 15, 245
QUPHAL	$P2_1212$	<i>Cryst. Growth Des.</i> 2010, 10, 2676
QUPHEP	$P2_1212$	<i>Cryst. Growth Des.</i> 2010, 10, 2676
QUSBIQ	$P6_222$	<i>Cryst. Growth Des.</i> 2010, 10, 146
RAKBIO	$P3_121$	<i>Z.Anorg.Allg.Chem.</i> 2001, 627, 1711
RAKBIO01/ RAKBIO02	$P3_121$	<i>Dalton Trans.</i> 2004, 21, 3440 <i>Inorg. Chem. Commun.</i> 2012, 26, 7
VACFOV	$P6_422$	<i>Angew. Chem. Int. Ed.</i> 2002, 41, 4471
VACFOV01	$P6_222$	<i>Dalton Trans.</i> 2013, 42, 10690
VACFUB	$P3_1$	<i>Angew. Chem. Int. Ed.</i> 2002, 41, 4471
VACFUB01	$P6_2$	<i>J. Coord. Chem.</i> 2009, 62, 2665
VIGDIY	$P3_221$	<i>Z.Kristallogr.</i> 1990, 193, 21
VUHHIQ	$P3_221$	<i>CrystEngComm.</i> 2009, 11, 746

References

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