

Combination between lacunary polyoxometalates and high-nuclear transition metal clusters under hydrothermal conditions: I. from isolated cluster to 1-D chain†

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The hydrothermal reactions of $[A-\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$ / $[A-\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and amines yielded four unprecedented hybrid high-nuclear Ni-substituted polyoxotungstates.

Polyoxometalates (POMs) exhibit an enormous variety of structures, which leads to interesting and unexpected properties that give rise to many applications in catalysis, medicine and magnetism.¹ Recently, lacunary Keggin or Dawson POMs have been attracted much attention because they can incorporate paramagnetic metals to form high-nuclear transition-metal-substituted POMs (TMSPs), resulting in unique magnetic properties.^{2,3} Compared with the large number of known TMSPs made by conventional solution syntheses at atmospheric pressure and relatively low temperature (below 100 °C), the investigation on the syntheses of the lacunary POM precursors combined with paramagnetic metal clusters under hydrothermal conditions remains largely undeveloped, though hydrothermal techniques have been widely applied to making POMs.⁴ Therefore, lacunary POM fragments combined with hydrothermal techniques may open a new avenue in making novel and unique TMSPs.

We chose trilacunary Keggin XW_9O_{34} fragments as the precursor based on the following considerations: (1) the trilacunary sites of XW_9O_{34} unit may act as the structure-directing agent and induce the paramagnetic metal ions to undergo large cluster aggregation under the rational hydrothermal conditions, which differs from the invisible structure-directing agent of lone pair electron in Se(IV) ;⁵ (2) the Keggin XW_9O_{34} and the large cluster aggregates formed *in-situ* may act as structural building units (SBUs) to combine subtly with each other, resulting in novel isolated or extended high-nuclear TMSPs. Here, we report the systematic syntheses and structures of four unprecedented high-nuclear TMSPs under hydrothermal conditions: $[\text{Ni}(\text{H}_2\text{O})_6][\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_6(\text{enMe})_3(B-\alpha\text{-SiW}_9\text{O}_{34})]_2 \cdot 8\text{H}_2\text{O}$ **1**, $[\text{Ni}(\text{enMe})_2][\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_6(\text{enMe})_3(B-\alpha\text{-SiW}_9\text{O}_{34})]_2 \cdot 10\text{H}_2\text{O}$ **2**, $[\text{Ni}(\text{enMe})_2(\text{H}_2\text{O})_2][\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_4(\text{enMe})_3(\text{CH}_3\text{COO})(B-\alpha\text{-PW}_9\text{O}_{34})]_2 \cdot 10\text{H}_2\text{O}$ **3** and $[\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_2(\text{dien})_3(B-\alpha\text{-PW}_9\text{O}_{34})] \cdot 4\text{H}_2\text{O}$ **4** (enMe = 1,2-diaminopropane, dien = diethylenetriamine), in which the hexanuclear $[\text{Ni}_6(\mu_3\text{-OH})_3]^{9+}$ cluster acts as a SBU and combines with trivacant XW_9O_{34} (X = Si, P) to form

TMSPs with isolated clusters and 1-D chain for **1–3** and **4**, respectively (Fig. 1). To date, though many lacunary Keggin polyoxotungstates incorporating Ni-clusters have been reported,⁶ the number of Ni ions in a single lacunary Keggin fragment is not more than four; while the number of Ni ions in **1–4** is six. Therefore, **1–4** not only are the first examples of hexa-substituted polyoxotungstates based on single lacunary Keggin fragments, but also contain the highest number of Ni ions in any known lacunary Keggin polyoxotungstate monomers.

Crystals of **1–4** were only obtained by hydrothermal reactions of $[A-\alpha\text{-XW}_9\text{O}_{34}]$, enMe/dien and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in sodium acetate buffer at 170 °C for 3 days,[‡] and not obtained by solution syntheses at atmospheric pressure. It is noteworthy that the amines used in the syntheses are a key point in the formation of **1–4**. In their absence attempts to make analogs of **1–4** proved fruitless under hydrothermal conditions. To explore di-/tri-amine influences on the structures, en (ethylenediamine), enMe and dien were used in the reactions. The experimental results show that similar POMs with **1–3** were also obtained in en-containing systems, while a novel 1-D chainlike POM, **4**, formed in the dien-containing system, respectively.

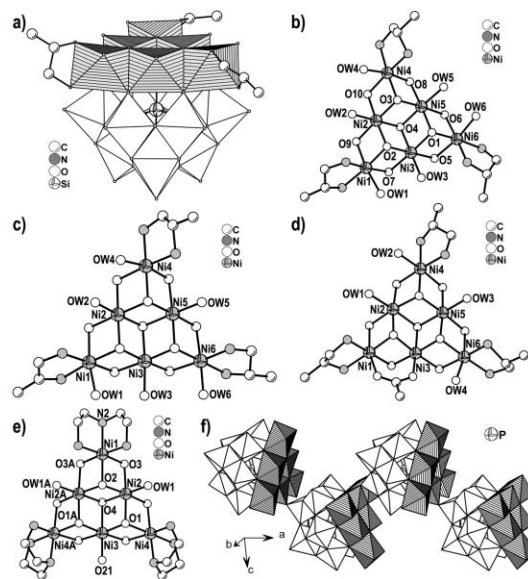


Fig. 1 (a) Polyhedral representation of polyoxoanion **1a**: WO_6 white; NiO_6 and NiO_4N_2 , lined shading. (b)–(e) Ball-and-stick representations of the Ni_6 units in **1–4**. The distances for Ni–N and Ni–O: 2.027(10)–2.098(10) and 1.947(7)–2.276(7) Å, respectively. (f) View of the 1D chain of **4** along the *a*-axis. The Ni–O–W angle is 136°.

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X-Ray analyses reveal that **1–4** contain the similar hexanuclear cluster core $[\text{Ni}_6(\mu_3\text{-OH})_3]^{9+}$ and trivacant XW_9O_{34} SBUs. Therefore, only the structure of **1** is described in detail. **1** consists of two large anions $[\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_6(\text{enMe})_3(B\text{-}\alpha\text{-SiW}_9\text{O}_{34})]^-$ **1a** (Fig. 1(a), S1, ESI[†]) and one $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ cation. **1a** can be described as a $B\text{-}\alpha\text{-}[\text{SiW}_9\text{O}_{34}]^{10-}$ unit capped by a triangle $[\text{Ni}_6(\mu_3\text{-OH})_3]^{9+}$, Ni_6 core comprising six Ni^{2+} ions and three hydroxyls (O1–O3) and further stabilized by three enMe, six H_2O and seven O (O4–O10) atoms (Fig. 1(b)) from $B\text{-}\alpha\text{-}[\text{SiW}_9\text{O}_{34}]^{10-}$ unit. In the triangular Ni_6 core, the Ni^{2+} ions can be divided into two groups according to the positions at which they are located: interior ($\text{Ni}2/\text{Ni}3/\text{Ni}5$) and exterior ($\text{Ni}1/\text{Ni}4/\text{Ni}6$) atoms. The three interior NiO_6 octahedra are located at the trivacant sites of $B\text{-}\alpha\text{-}[\text{SiW}_9\text{O}_{34}]^{10-}$; while the three exterior NiO_4N_2 octahedra are further attached to interior Ni_3 triad unit by edge-sharing to form a novel Ni_6 aggregate. It is also understood that the Ni_6 core is linked by three truncated cubanes of $\{\text{Ni}_3\text{O}_4\}$ *via* sharing one edge with each other, and all sharing a common vertex ($\mu_4\text{-O}4$). To our knowledge, such a Ni_6 cluster core has not been reported so far. BVS calculations⁷ reveal that the range of bond valences for the six terminal O atoms of Ni sites is 0.27–0.32, strongly suggesting diprotonation for all of them; while the bond valences of the three $\mu_3\text{-O}$ (O1–O3) are 1.11, 1.09 and 1.05, respectively, indicating monoprotonation.^{6b,c} This is also consistent with the overall charge balance of **1**. It is noted that **1a** only has a mono-negative charge, thus exhibiting an unusually low charge density.

Notably, the coordination environments of the Ni_6 core in **1** and **2** are different owing to different orientations of some water ligands, resulting in two isomeric hybrid Ni_6 units (Fig. 1(b), (c)). These water ligands may further be substituted, *e.g.* intra- and inter-molecular linkage through multidentate ligands as well as intermolecular concentration, leading to novel or extended structures. Fortunately, such TMSPs **3** and **4** were successfully obtained *via* intramolecular linkage modes in our experiments. As shown in Fig. 1(d), the hybrid Ni_6 unit in **3** can be derived from that of **2** by replacing two water ligands on Ni1 and Ni3 ions with one bidentate acetate anion. The bridging acetate ligand in **3** makes the $\text{Ni}1 \cdots \text{Ni}3$ distance (2.937(3) Å) not only shorter than that of other $\text{Ni} \cdots \text{Ni}$ (3.094(3)–3.160(3) Å) of Ni_6 core in **3** but also shorter than that of all $\text{Ni} \cdots \text{Ni}$ (3.030(2)–3.160(3) Å) of Ni_6 cores in **1–4**, which might lead to a relatively stronger magnetic exchange interaction.

The hybrid Ni_6 unit in **4**, possessing C_s symmetry with N2, O2, O4, O21, Ni1 and Ni4 atoms lying on the mirror plane (Fig. 1(e)), is also transferred from that of **1** or **2** by replacing all enMe and water ligands on three exterior Ni ions with three tridentate dien ligands. Such a hybrid Ni_6 unit caps on one $[B\text{-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ anion to form a neutral cluster $[\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_3(\text{dien})_3(B\text{-}\alpha\text{-PW}_9\text{O}_{34})]$ (**4a**). Also, the water ligand on the interior Ni3 ion of **4a** is further replaced by one terminal O21 atom of one WO_6 octahedron from one adjacent **4a** cluster (Fig. 1(e)), forming the first extended TMSP with a 1-D zigzag chain made of Ni_6 and PW_9O_{34} SBUs *via* corner-sharing (O21) between NiO_6 and WO_6 octahedra *via* intermolecular interactions (Fig. 1(f)).

It is notable that, because there is a single independent anion in a general position with the cation situated on a centre of symmetry, the ratio of cation : anion in **1–3** is 1 : 2. Additionally, although the $[A\text{-}\alpha\text{-XW}_9\text{O}_{34}]^{9-}$ ($X = \text{Si}, \text{P}$) ions were used as starting material, all the products contain $[B\text{-}\alpha\text{-XW}_9\text{O}_{34}]^{9-}$ units, indicating that the isomerizations $[A\text{-}\alpha\text{-XW}_9\text{O}_{34}]^{10-} \rightarrow [B\text{-}\alpha\text{-XW}_9\text{O}_{34}]^{10-}$ and

$[A\text{-}\alpha\text{-PW}_9\text{O}_{34}]^{9-} \rightarrow [B\text{-}\alpha\text{-PW}_9\text{O}_{34}]^{9-}$ must have taken place during the course of the reactions. The later has also been observed under conventional solution methods.^{6e}

Since **1–4** contain a similar Ni_6 core, only **3** and **4** were selected as examples for magnetic characterization. The magnetic susceptibilities of **3** and **4** were measured at 2–300 K and are shown in Fig. 2. The experimental $\chi_m T$ values of **3** and **4** at room temperature are 17.59 and 8.27 $\text{cm}^3 \text{mol}^{-1} \text{K}$ per formula unit, respectively, which are expected for thirteen and six uncoupled high-spin Ni^{2+} ion with $g > 2$.⁸ Upon cooling, the $\chi_m T$ values of **3** and **4** increase to a maximum of 45.9 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 11 K and 22.5 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 8.5 K, respectively, then decreasing sharply, which might be mainly attributed to the presence of zero-field splitting (ZFS). The behavior suggests that there exist overall ferromagnetic interactions with the presence of ZFS for Ni^{2+} ions in both cases. The temperature dependence of the reciprocal susceptibilities ($1/\chi_m$) obeys the Curie–Weiss law above 40 K for **3** and 50 K for **4** with $\theta = 23.8$ and 24.9 K (Fig S2, ESI[†]), respectively, which support the presence of overall ferromagnetic coupling between the Ni^{2+} ions of both cases. AC magnetic susceptibilities of **3** and **4** at 111, 511, 911, 1511 and 2511 Hz were measured under $H_{ac} = 3$ Oe, and no frequency dependence was observed. To analyze the observed magnetic properties, the exchange schemes 1 and 2 (inset of Fig. 2) are used for **3** and **4**, respectively, where the numbering corresponds to that of Fig. 1(d), (e) except that 5 and 6 in scheme 2 correspond to Ni2A and Ni4A in Fig. 1(e). Considering the C_{2v} symmetry of the Ni_6 core in **4**, only five J parameters are used. The magnetic data of **3** and **4** are simulated based on the spin Hamiltonians in eqn (1) and (2), respectively, using the package MAGPACK,⁹ where D is the ZFS parameter and the contribution of the mononuclear Ni^{2+} species in **3** is incorporated through the Curie law.

$$\hat{H} = -2J_1\hat{S}_1\hat{S}_2 - 2J_2\hat{S}_1\hat{S}_3 - 2J_3\hat{S}_2\hat{S}_3 - 2J_4\hat{S}_2\hat{S}_4 - 2J_5\hat{S}_2\hat{S}_5 - 2J_6\hat{S}_3\hat{S}_5 - 2J_7\hat{S}_3\hat{S}_6 - 2J_8\hat{S}_4\hat{S}_5 - 2J_9\hat{S}_5\hat{S}_6 + \sum D_i\hat{S}_{iz}^2 \quad (1)$$

$$\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3) - 2J_2\hat{S}_2\hat{S}_5 - 2J_3(\hat{S}_2\hat{S}_4 + \hat{S}_5\hat{S}_6) - 2J_4(\hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_5) - 2J_5(\hat{S}_3\hat{S}_4 + \hat{S}_3\hat{S}_6) + \sum D_i\hat{S}_{iz}^2 \quad (2)$$

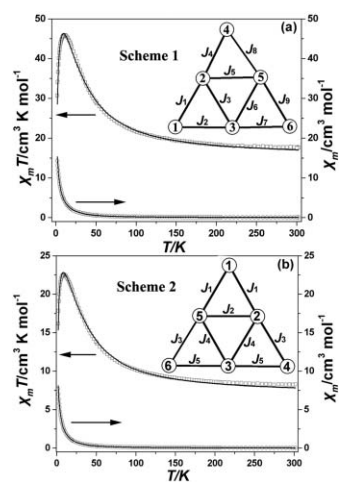


Fig. 2 Temperature dependence of χ_m (○) and $\chi_m T$ (□) values for **3** (a) and **4** (b). The solid lines correspond to the best-fit curves using the parameters described in the text.

The best-fit parameters obtained are $J_1 = 0.47 \text{ cm}^{-1}$, $J_2 = 0.75 \text{ cm}^{-1}$, $J_3 = 1.23 \text{ cm}^{-1}$, $J_4 = 0.47 \text{ cm}^{-1}$, $J_5 = 1.23 \text{ cm}^{-1}$, $J_6 = 1.23 \text{ cm}^{-1}$, $J_7 = 0.43 \text{ cm}^{-1}$, $J_8 = 0.47 \text{ cm}^{-1}$, $J_9 = 0.43 \text{ cm}^{-1}$, $g = 2.24$, $D = 1.58 \text{ cm}^{-1}$ and $R = 2.70 \times 10^{-4}$ for **3**, and $J_1 = 0.60 \text{ cm}^{-1}$, $J_2 = 1.26 \text{ cm}^{-1}$, $J_3 = 0.64 \text{ cm}^{-1}$, $J_4 = 1.28 \text{ cm}^{-1}$, $J_5 = 0.63 \text{ cm}^{-1}$, $g = 2.14$, $D = 0.52 \text{ cm}^{-1}$ and $R = 2.57 \times 10^{-4}$ for **4** (R is defined as $\sum[(\chi_m T)_{\text{obs}} - (\chi_m T)_{\text{calc}}]^2 / \sum[(\chi_m T)_{\text{obs}}^2]$). The results confirm that all the Ni \cdots Ni interactions in both Ni $_6$ cores are ferromagnetic, in accord with the Ni–O–Ni angles in both cases in the 90–104° region, a range in which Ni \cdots Ni ferromagnetic exchange pathways are dominant (90 ± 14°).¹⁰

The magnetization curves $M(H)$ of **3** and **4** (Fig S3, ESI†) at $T = 2 \text{ K}$ exhibit a rapid increase at low field and tend to reach the saturation state at about 7 and 3 T with values of $27.6N\beta$ and $12.8N\beta$ for **3** and **4** at 7 T, respectively, as expected for systems of two Ni $_6$ ($S = 6$) cores and one mononuclear ($S = 1$) species (**3**), as well as one Ni $_6$ ($S = 6$) unit (**4**) with ferromagnetic interactions. The theoretical magnetization curves of **4** based on the above fitting parameters reproduces the experimental data well; the lower experimental data of **3** at high field may be due to the larger zero-field splitting effect of Ni $^{2+}$ ions in **3**.

In summary, four novel TMSPs, from isolated to 1-D chains, were successfully made under hydrothermal conditions. The key points of the synthetic procedures have been well established, and indicate that hydrothermal techniques can offer an effective way for making lacunary POMs incorporated with high-nuclear transition metal clusters. In addition, the trilacunary sites of the XW $_9$ O $_{34}$ unit can act as a structure-directing agent that first captures a trimeric metal cluster (e.g. [Ni $_3(\mu_3\text{-OH})_3(\text{H}_2\text{O})_3$] core containing Ni $_2$, Ni $_3$ and Ni $_5$ atoms in Fig. 1(b)) for completing Keggin POM and then further aggregating to form high-nuclear TMSPs. Future work is in progress to make other new TMSPs built from larger metal cluster aggregates and other types of lacunary precursors (e.g. [XW $_{10}$ O $_{36}$] $^{n-}$ and [X $_2$ W $_{15}$ O $_{56}$] $^{m-}$) or mixed multi-lacunary precursors under hydrothermal conditions.

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Notes and references

‡ *Synthesis of 1–4*: Na $_{10}[A-\alpha\text{-SiW}_9\text{O}_{34}]_n\text{H}_2\text{O}$ (SiW $_9$) and Na $_9[A-\alpha\text{-PW}_9\text{O}_{34}]_n\text{H}_2\text{O}$ (PW $_9$) were prepared by literature method.¹¹ A mixture of SiW $_9$ (0.30/0.80 g for **1/2**) or PW $_9$ (0.30/1.10 g for **3/4**), enMe (0.30/0.10/0.30 ml for **1/2/3**) or dien (0.30 ml for **4**) and NiCl $_2\cdot 6\text{H}_2\text{O}$ (0.80/0.20/0.80/0.80 g for **1/2/3/4**) was added with stirring in 10 ml of a 0.5 M sodium acetate buffer (pH 4.8). This solution was sealed in a 35 mL bomb with a Teflon liner, heated at 170 °C for 3 d and then cooled to room temperature. Accordingly, green prismatic crystals of **1–4** were obtained. Anal. Calc. (found %) for C $_{18}$ H $_{118}$ N $_{12}$ Ni $_{13}$ O $_{100}$ Si $_2$ W $_{18}$ **1**: C, 3.47 (3.32); H, 1.91 (2.23); N, 2.70 (2.52); for C $_{24}$ H $_{130}$ N $_{16}$ Ni $_{13}$ O $_{96}$ Si $_2$ W $_{18}$ **2**: C, 4.57 (4.48); H, 2.08 (2.17); N, 3.55 (3.43); for C $_{28}$ H $_{132}$ N $_{16}$ Ni $_{13}$ O $_{98}$ P $_2$ W $_{18}$ **3**: C, 5.26 (4.97); H, 2.08 (2.36); N, 3.50 (3.39); for C $_{12}$ H $_{54}$ N $_9$ Ni $_6$ O $_{43}$ PW $_9$ **4**: C, 4.72 (4.76); H, 1.78 (1.92); N, 4.13 (3.99).

§ *Crystal data*: for **1**: $M_r = 6231.95$, monoclinic, $P2_1/n$, $a = 13.9166(8)$, $b = 24.2125(12)$, $c = 18.0515(11) \text{ \AA}$, $\beta = 109.117(3)^\circ$, $V = 5747.1(6) \text{ \AA}^3$, $Z = 2$, $D_c = 3.601 \text{ g cm}^{-3}$, $\mu = 20.135 \text{ mm}^{-1}$, $F(000) = 5668$, GOF = 1.058, a total of 41855 reflections were collected, 13003 of which were unique ($R_{\text{int}} = 0.0566$). R_1 (wR_2) = 0.0448 (0.1109) for 775 parameters and 11412 reflections ($I > 2\sigma(I)$). For **2**: $M_r = 6308.15$, monoclinic, $P2_1/n$, $a = 16.017(4)$, $b = 22.536(5)$, $c = 17.176(4) \text{ \AA}$, $\beta = 103.655(4)^\circ$, $V = 6025(2) \text{ \AA}^3$, $Z = 2$, $D_c = 3.477 \text{ g cm}^{-3}$, $\mu = 19.208 \text{ mm}^{-1}$, $F(000) = 5756$, GOF = 1.021, a total of 43795 reflections were collected, 13658 of which were unique ($R_{\text{int}} = 0.0538$). R_1 (wR_2) = 0.0434 (0.1088) for 813 parameters and 11726

reflections ($I > 2\sigma(I)$). For **3**: $M_r = 6395.97$, monoclinic, $P2_1/n$, $a = 15.503(3)$, $b = 23.240(5)$, $c = 18.428(4) \text{ \AA}$, $\beta = 107.110(4)^\circ$, $V = 6346(2) \text{ \AA}^3$, $Z = 2$, $D_c = 3.347 \text{ g cm}^{-3}$, $\mu = 18.247 \text{ mm}^{-1}$, $F(000) = 5844$, GOF = 1.095, A total of 48285 reflections were collected, 14398 of which were unique ($R_{\text{int}} = 0.0453$). R_1 (wR_2) = 0.0444 (0.1253) for 856 parameters and 12229 reflections ($I > 2\sigma(I)$). For **4**: $M_r = 3050.52$, orthorhombic, $Prma$, $a = 16.4477(3)$, $b = 19.4046(3)$, $c = 16.2221(1) \text{ \AA}$, $V = 5177.5(1) \text{ \AA}^3$, $Z = 4$, $\rho = 3.914 \text{ g cm}^{-3}$, $\mu = 22.171 \text{ mm}^{-1}$, $F(000) = 5528$, GOF = 1.188, a total of 28615 reflections were collected, 5354 of which were unique ($R_{\text{int}} = 0.0594$). R_1 (wR_2) = 0.0409 (0.0826) for 398 parameters and 4708 reflections ($I > 2\sigma(I)$).

Data were collected on a SMART-CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The program SADABS was used for the absorption correction. The structures **1–4** were solved by the direct method and refined on F^2 by full-matrix least-squares methods using the SHELXL97 program package. The Ni7, C4-5, C7-9 and OW7-9 atoms in **1**, the C1-6 atoms in **2**, the C2-3, C6 and C11 atoms in **3**, and the C1-2 atoms in **4** are disordered over two sites. Detailed information is provided in Fig. S7–S15, ESI† CCDC 622063–622066. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617191e.

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