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# Transformation of maleato manganese(II): temperature effect and coordination modes ☆

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## Abstract

Two maleato bipyridine manganese(II) coordination polymers $[Mn(male)(bpy)(H_2O)]_n \cdot 2nH_2O$ (**1**) and $[Mn(male)(bpy)]_n$ (**2**) ($H_2male$ = maleic acid, bpy = 2,2′-bipyridine) were prepared in an ice-bath and at room temperature respectively, and were spectroscopically and structurally characterized. Complex **1** obtained at low temperature, possesses a one-dimensional helical chain in the solid state with hepta-coordination number at the manganese center. At room temperature, the hydrated complex **1** was irreversibly converted into the thermodynamically stable dehydrated product **2** with octahedral coordination. A similar dehydration effect was observed for the maleato manganese(II) complex with a more conjugated phenanthroline (phen) ligand. The maleato manganese(II) coordination polymer $[Mn(male)(phen)]_n \cdot nH_2O$ (**3**) can be converted into the dehydrated product $[Mn(male)(phen)]_n$ (**4**) upon heating, while the resultant product retains a similar pattern of coordination mode.

*Keywords:* Manganese maleate; Coordination polymer; Temperature effect; Helical architecture; Hydrogen bonds; π–π interactions

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## 1. Introduction

Metal-directed self-assembly of coordination polymers with well-defined architectures has presently been one topic of intense interest in the field of supra-molecular chemistry owing to their original topologies, desired properties and potential applications in multidisciplinary areas, e.g., catalysis, nonlinear optics, magnetism, luminescence, gas storage and chemical absorption [1]. Considerable efforts have been made to construct such extended solid materials with manipulated and tunable functionalities. The most common used strategy is to employ appropriate organic building blocks with several metal centers through direct bond formation. However, it still remains a challenge for synthetic chemists to predict and control the way of molecular components assembled in the crystalline phase. This is because the self-assembly processes are heavily influenced by subtle factors, such as templates [2], choice of solvents and counterions [3], and pH values [4]. When the reaction conditions are deliberately controlled, infinite networks with novel topologies can be gained. Though it was clear long ago that temperature can dramatically affect the extended structure of the networks, the influence of temperature in the formation of coordination polymers is less well understood and systematic studies are rare [5]. It is known that in the self-assembly of both synthetic and biological systems the thermodynamic product is usually favored, the kinetic product may also be obtained if the shape of the energy hypersurface is such that the system becomes trapped in local minima [6]. To develop the better understanding of temperature effects on the formation of coordination polymers, in the present contribution, two new maleato manganese(II) polymers formulated as $[Mn(male)(bpy)(H_2O)]_n \cdot 2nH_2O$ (**1**) and $[Mn(male)\ (bpy)]_n$ (**2**) were temperature-dependently prepared and structurally characterized. Irreversible conversion from kinetic maleato manganese **1** to the dehydrate product **2** was investigated.

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## 2. Experimental

All chemicals were commercially available and used without further purification. Elemental microanalyses (C, H and N) were performed on an EA 1100 elemental analyzer. Infrared spectra were recorded from KBr pellets on a Nicolet FT-IR 360 spectrophotometer in the range of 4000–400 cm$^{-1}$.

### 2.1. Preparation of [Mn(male)(bpy)(H$_2$O)]$_n$ · 2nH$_2$O (1)

Manganese maleate was prepared in situ at 0 °C by mixing $MnCl_2 \cdot 4H_2O$ (0.99 g, 5 mmol) and an equimolar amount of sodium maleate, dissolving in 20 ml double distilled water. After stirring the mixture for 15 min, an equimolar amount of 2,2′-bipyridine (0.780 g, 5 mmol), dissolved in 10 ml methanol, was slowly added and stirring was continued for another 10 min. The solution was kept in the refrigerator. Block-like crystals suitable for single crystal diffraction analysis were obtained a few days later. Yield: 85%. *Anal.* Calcd. for $C_{14}H_{16}N_2O_7Mn$: C, 44.3; H, 4.2; N, 7.4. Found: C, 43.0; H, 4.1; N, 7.3%. IR (KBr, cm$^{-1}$): $\nu$(O–H) $3377_{vs}$, $\nu_{as}$(C=O) $1578_{vs}$, $\nu_s$(C=O) $1439_s$, $\nu$(Mn–O) $773_s$.

### 2.2. Preparation of [Mn(male)(bpy)]$_n$ (2)

The preparation of **2** was similar to the hydrate product **1** except the reaction was proceeded at ambient temperature. Plate single crystals suitable for X-ray diffraction were obtained after a few weeks. Yield: 90%. *Anal.* Calcd. for $C_{14}H_{10}N_2O_4Mn$: C, 51.7; H, 3.1; N, 8.6. Found: C, 52.2; H, 3.2; N, 8.9%. IR (KBr, cm$^{-1}$): $\nu_{as}$(C=O) $1593_s$, $1547_{vs}$, $\nu_s$(C=O) $1429_m$, $1398_m$, $\nu$(Mn–O) $774_m$.

### 2.3. Conversion of [Mn(male)(bpy)(H$_2$O)]$_n$ · 2nH$_2$O (1) to [Mn(male)(bpy)]$_n$ (2)

The crystals of **1** were picked out and put in a beaker with some mother liquid at ambient temperature. A few days later, the block-like yellow crystals segmented into ‘chaos’ and IR spectra justified it was converted into thermodynamic product **2**.

### 2.4. Conversion of [Mn(male)(phen)]$_n$ · nH$_2$O (3) to [Mn(male)(phen)]$_n$ (4)

The maleato phenanthroline manganese complexes **3** and **4** were prepared as reported very recently [7]. Crystals of **3** (0.37g, 1 mmol) in 5 ml water were warmed in a 50 °C warm bath for 8 h. The resultant product was showed to be the dehydrated maleato manganese complex **4** by IR spectra.

### 2.5. X-ray data collection, structure solution and refinement

Intensity data were collected on a Bruker SMART APEX CCD using Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). Both structures were solved by direct methods and refined by full-matrix least squares based on $F^2$ using

Table 1
Crystallographic data for [Mn(male)(bpy)(H$_2$O)]$_n$ · 2nH$_2$O (**1**) and [Mn(male)(bpy)]$_n$ (**2**)

| Compounds | 1 | 2 |
|---|---|---|
| Empirical formula | $C_{14}H_{16}N_2O_7Mn$ | $C_{14}H_{10}N_2O_4Mn$ |
| Formula weight | 379.23 | 325.18 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| $a$ (Å) | 8.0194(2) | 11.4546(3) |
| $b$ (Å) | 8.6486(1) | 13.3064(4) |
| $c$ (Å) | 23.3306(4) | 8.8076(3) |
| $\beta$ (°) | 92.059(1) | 111.455(1) |
| $V$ (Å$^3$) | 1617.09(5) | 1249.42(7) |
| $Z$ | 4 | 4 |
| $D_{calcd.}$ (g cm$^{-3}$) | 1.558 | 1.729 |
| Crystal size (mm) | $0.061 \times 0.051 \times 0.035$ | $0.066 \times 0.200 \times 0.216$ |
| $F_{000}$ | 780 | 660 |
| $\theta$ range (°) | $1.75 \leqslant \theta \leqslant 28.82$ | $1.91 \leqslant \theta \leqslant 28.94$ |
| $T$ (K) | 296 | 296 |
| μ (mm$^{-1}$) | 0.855 | 1.075 |
| $R[I > 2\sigma(I)]$ | $R = 0.0554$, $R_w = 0.1499$ | $R = 0.0383$, $R_w = 0.0816$ |
| $R$ (all data) | $R = 0.0595$, $R_w = 0.1553$ | $R = 0.0524$, $R_w = 0.0865$ |
|  | $w^{-1} = \sigma^2(F_o^2) + 0.1245P^2$ $P = (F_o^2 + 2F_c^2)/3$ | $w^{-1} = \sigma^2(F_o^2) + 0.0373P^2 + 0.1049P$, $P = (F_o^2 + 2F_c^2)/3$ |
| Goodness-of-fit | 0.912 | 1.027 |
| Minimum and maximum residual density (e Å$^{-3}$) | −1.130 and 0.727 | −0.345 and 0.335 |

Table 2
Selected bond lengths (Å) and angles (°) for 1$^{a}$ and 2$^{b}$

| | | | | | |
|---|---|---|---|---|---|
| *[Mn(male)(bpy)(H$_2$O)]$_n$ · 2nH$_2$O (**1**)* | | | | | |
| *Bond lengths* | | | | | |
| Mn1–O1 | 2.3666(2) | Mn1–O2 | 2.2344(2) | Mn1–O3$^{i}$ | 2.362(2) |
| Mn1–O4$^{i}$ | 2.3600(2) | Mn1–Ow1 | 2.1375(2) | Mn1–N1 | 2.2528(2) |
| Mn1–N2 | 2.2540(2) | | | | |
| *Bond angles* | | | | | |
| O1–Mn1–O2 | 56.67(5) | O1–Mn1–O3$^{i}$ | 137.79(6) | O1–Mn1–O4$^{i}$ | 158.97(7) |
| O1–Mn1–O1w | 82.99(6) | O1–Mn1–N1 | 88.21(6) | O1–Mn1–N2 | 97.58(6) |
| O2–Mn1–O3$^{i}$ | 84.96(6) | O2–Mn1–O4$^{i}$ | 139.62(6) | O2–Mn1–O1w | 95.68(7) |
| O2–Mn1–N1 | 139.66(6) | O2–Mn1–N2 | 91.65(6) | O3–Mn1–O4 | 54.67(7) |
| O3–Mn1–O1w$^{i}$ | 84.23(7) | O3–Mn1–N1$^{i}$ | 133.59(7) | O3$^{i}$–Mn1–N1$^{i}$ | 100.36(6) |
| O4–Mn1–Ow1$^{i}$ | 81.97(7) | O4–Mn1–N1$^{i}$ | 79.80(6) | O4–Mn1–N2$^{i}$ | 94.97(7) |
| Ow1–Mn1–N1 | 99.23(7) | Ow1–Mn1–N2 | 171.69(7) | N1–Mn1–N2 | 72.57(6) |
| *Hydrogen bonding* | | | | | |
| *Bond lengths* | | | | | |
| O1w···O2$^{i}$ | 2.727(3) | O1w···O3w | 2.730(2) | O2w···O1$^{ii}$ | 2.810(3) |
| O2w···O4$^{iii}$ | 2.756(3) | O2w···O2w$^{ii}$ | 2.863(3) | O3w···O4$^{iv}$ | 2.805(4) |
| *[Mn(male)(bpy)]$_n$ (**2**)* | | | | | |
| *Bond lengths* | | | | | |
| Mn1–O1 | 2.1812(2) | Mn1–O2$^{i}$ | 2.1499(2) | Mn1–O3 | 2.1157(2) |
| Mn1–O4$^{ii}$ | 2.1733(2) | Mn1–N1 | 2.2688(2) | Mn1–N2 | 2.3286(2) |
| *Bond angles* | | | | | |
| O1–Mn1–O2$^{i}$ | 94.16(7) | O1–Mn1–O3 | 82.89(6) | O1–Mn1–O4$^{ii}$ | 176.65(6) |
| O1–Mn1–N1 | 86.74(6) | O1–Mn1–N2 | 93.61(6) | O2–Mn1–O3$^{i}$ | 99.63(6) |
| O2$^{i}$–Mn1–O4$^{ii}$ | 84.15(6) | O2–Mn1–N1$^{i}$ | 89.82(6) | O2–Mn1–N2$^{i}$ | 159.24(7) |
| O3–Mn1–O4$^{ii}$ | 94.53(6) | O3–Mn1–N1 | 166.42(6) | O3–Mn1–N2 | 100.42(6) |
| O4$^{ii}$–Mn1–N1 | 96.14(6) | O4$^{ii}$–Mn1–N2 | 88.95(6) | N1–Mn1–N2 | 71.44(7) |

[a] Symmetry transformation: (i) $1-x, 1/2+y, 1/2-z$; (ii) $1-x, -y, -z$; (iii) $-1+x, -1/2-y, -1/2+z$; (iv) $x, 1+y, z$.

[b] Symmetry transformation: (i) $x, 1/2-y, 1/2+z$; (ii) $1-x, -y, 1-z$.

SHELX-97 software [8]. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included at geometrically calculated positions with thermal parameters derived from the parent atoms, except those bonded to the water molecules. The water hydrogen atoms were located in the difference map and included at these sites, with a fixed isotropic displacement factor of $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{O})$. Crystal data, data collection and refinement parameters are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

## 3. Results and discussion

Based on IR spectra, we can deliberately diagnose the coordination nature of the maleato group in complexes **1** and **2**. Specifically, asymmetric stretching vibrations $\nu_{\mathrm{as}}(\mathrm{COO})$ appear near 1578 cm$^{-1}$ for **1** and between 1593 and 1547 cm$^{-1}$ for **2**, and the symmetric stretching vibrations $\nu_{\mathrm{s}}(\mathrm{COO})$ are observed near 1439 cm$^{-1}$ for **1** and between 1429 and 1398 cm$^{-1}$ for **2**. The separations $[\nu_{\mathrm{as}}(\mathrm{COO})-\nu_{\mathrm{s}}(\mathrm{COO})]$ of complexes **1** and **2** (139 and 118 cm$^{-1}$) are much smaller than the value of 200 cm$^{-1}$ for the free maleato group, indicating that the coordinated carboxyl group is in a bidentate bridging or chelating mode [9,10].

X-ray diffraction analysis reveals the maleato manganese dihydrate **1** possesses 1D helical chains with the basic building unit Mn(male)(bpy)(H$_2$O). Each manganese atom is primarily coordinated by four oxygen atoms from two bidentated maleates, two nitrogen atoms from bpy and one water molecule, in an irregular pentagonal-bipyramidal configuration (Fig. 1). The carboxyl oxygen atoms O1, O2 chelate to central manganese with an O1–Mn1–O2 bond angle of 56.7°, while O3, O4 of the other carboxyl group bind another manganese center. Thus each maleato unit serves as a bis(bidentate) ligand to link two manganese atoms and yields a half turn of the helical structure. All the carbon atoms of the maleato unit form a common plane, from which both terminal carboxyl groups O1–C1–O3 and O3–C4–O4 are twisted from the carbon backbone by 20.0° and 72.1°, respectively. The four Mn–O bond distances are different from each other to some extent (Table 2), with that to O2 being particularly short [2.2344(2) Å]. Unexpectedly, the shortest bond distance is that to the coordinated water molecule [Mn1–O1w 2.1375(2) Å]. So far, a great majority of structurally characterized Mn(II) complexes take invariably a

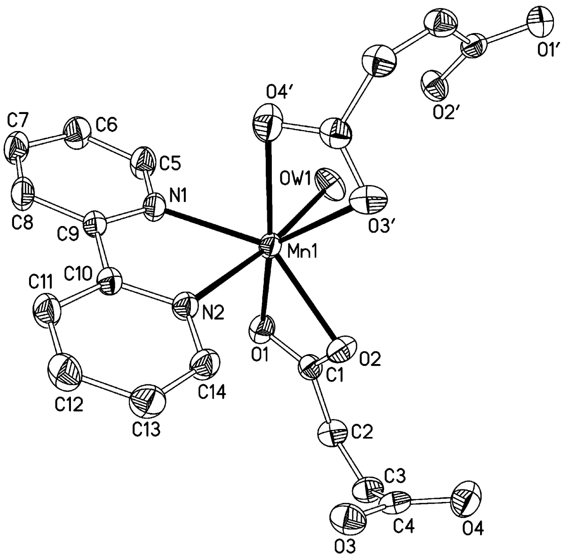


Fig. 1. One of the asymmetric units of $[Mn(male)(bpy)(H_2O)]_n \cdot 2nH_2O$ (**1**) in the Λ-configuration; hydrogen atoms and water molecules were omitted for clarity; thermal ellipsoids are drawn at 30% probability.

six-coordinate octahedral geometry around the metal atom. Complexes with coordination numbers exceeding six are limited to a few examples [11]. To the best of our knowledge, a helical coordination polymer based on a hepta-coordinated manganese center has not yet been documented hitherto. Extension of the basic building unit along the crystallographic $2_1$ axis in the *b* direction gives an infinite 1D helical architecture with a long pitch of 8.649 Å. The helical chain is decorated by 2,2′-bpy ligands alternatively at the two sides and the 2,2′-bpy planes on the same side are absolutely parallel one another, while they have a dihedral angle of 42.8° with those on the other side (Fig. 2). The helical chains are further extended through hydrogen bonds between water molecules and carboxyl oxygen atoms into a two-dimensional network.

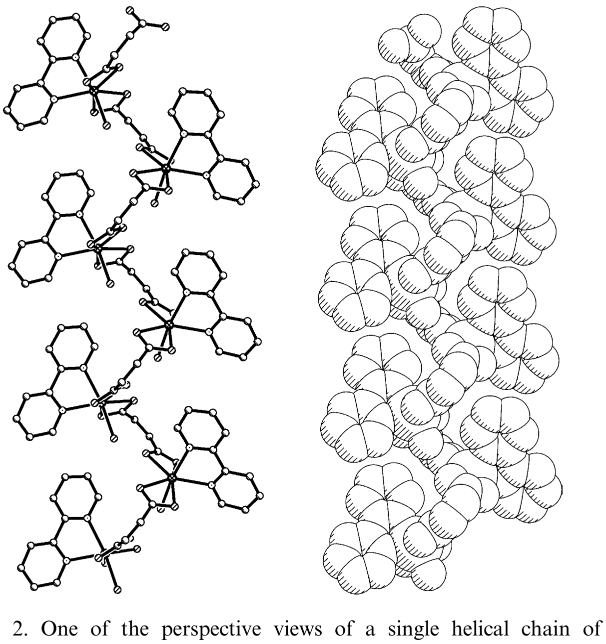


Fig. 2. One of the perspective views of a single helical chain of $[Mn(male)(bpy)(H_2O)]_n \cdot 2nH_2O$ (**1**) in the M-configuration.

The asymmetric unit of **2** consists of one manganese center, one maleato group and one bpy ligand. Each manganese center primarily coordinates to two nitrogen atoms from 2,2′-bpy and four carboxylate oxygen atoms from three maleato groups, in a geometry which is best described as a distorted octahedron (Fig. 3). The Mn1–N1 bond distance [2.2688(2) Å] is slightly shorter than the Mn1–N2 bond [2.3286(2) Å] in the same ligand, suggesting some twist in the 2,2′-bpy ligand (dihedral angle 11.5° between the two pyridyl rings). *Cis*-fashioned oxygen atoms O1 and O3 at the two termini of the maleato unit bind the manganese center into a seven-member chelate ring with an O1–Mn1–O3 bond angle of 82.89°, while O2 and O4 bind to the other two manganese atoms. In this way, each maleato group acts as a tetradentate ligand to coordinate three manganese atoms. The dihedral angle (45.0°) between O1–C1–O3 and O3–C4–O4 is much smaller than that in **1** (67.9°). Both terminal carboxyl groups O1–C1–O2 and O3–C4–O4 twist from the carbon backbone C1–C2–C3–C4 by 45.9°and 1°, respectively. The conformations of the maleato units in the two complexes are so different that the explanation why two different topological products were obtained becomes obvious. The coordination mode of the maleato group is to some extent similar to those previously reported for $[Mn_4(male)_2(bpy)_8](ClO_4)_4 \cdot (MeOH)_2(H_2O)_2$ [12], $[Mn(male)(\mu\text{-}4,4'\text{-bpy})]_n \cdot 0.5nH_2O$ [13] and $[Mn(male)(phen)]_n$ [7,14]. However, the extension of the basic unit and the packing style are different from those related compounds, thus giving rise to topologically different products. In addition, dimeric $[Mn_2(male)_2(bpy)_2]$ may

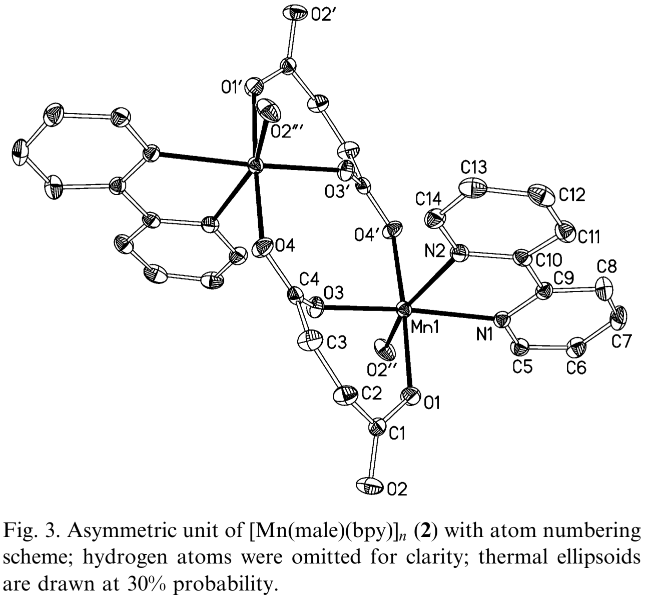
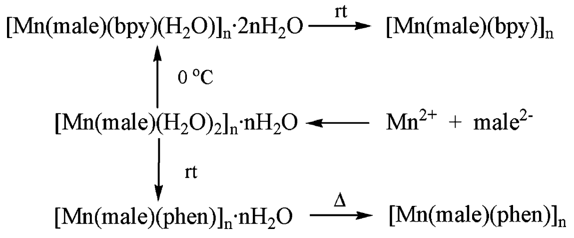


Fig. 3. Asymmetric unit of $[Mn(male)(bpy)]_n$ (**2**) with atom numbering scheme; hydrogen atoms were omitted for clarity; thermal ellipsoids are drawn at 30% probability.

be better as a secondary building unit (SBU) than monomeric [Mn(male)(bpy)] for clearly describing the crystal structure. In the dimeric model, the extension directions of O2 and O2′, O2″ and O2‴ are opposite to each other, respectively, linking and being linked by another four SBUs into a two-dimensional zigzag structure. π–π stacking interactions between bipyridyl planes further extend the two-dimensional structure into a three-dimensional network.

The formation of both maleato manganeses complexes is temperature-dependent. When the reaction proceeded at 0 °C, only the one-dimensional coordination polymer **1** was separated. Whereas at ambient temperature, only the thermodynamic product **2** was isolated. Furthermore, the irreversible conversion from **1** to **2** was observed when **1** was exposed to an ambient temperature for a few days and this reaction could be qualitatively traced by IR spectra. As to the details of how the conversion proceeds requires further theoretical deduction and kinetic measurements. Here the possible mechanism of transformation is depicted as follows. In the first step, the manganese maleate species $[Mn(male)(H_2O)_2]_n \cdot nH_2O$ was formed according to previous reports [15]. Addition of 2,2′-bipyridine ligand replaces the water molecules to complete the formation of the kinetic product $[Mn(male)(bpy)(H_2O)]_n \cdot 2nH_2O$ (**1**) with hepta-coordination. On warming to room temperature, the maleato manganese complex **1** was further compelled into the thermodynamically stable product $[Mn(male)(bpy)]_n$ **2** with dehydration. Very recently, the stable maleato bipyridine manganese species **2** has been separated as the only product in the $Mn^{2+}$/maleate/bipyridine system in ethanol solution [7]. However, a similar condition with phenanthroline results in the formation of the hydrated product $[Mn(male)(phen)]_n \cdot nH_2O$ (**3**), which can be converted into the dehydrated maleato phenanthroline manganese(II) $[Mn(male)(phen)]_n$ (**4**) [7,14] upon heating in our experiment. This is much related, but having the more conjugated phenanthroline ring in the complexes. The detailed transformations of the maleato manganese complexes is shown in Scheme 1.



Scheme 1. Transformations of maleato manganese complexes with 2,2-bipyridine and phenanthroline groups.

## 4. Supplementary materials

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 215790 for compound **1** and 215791 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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