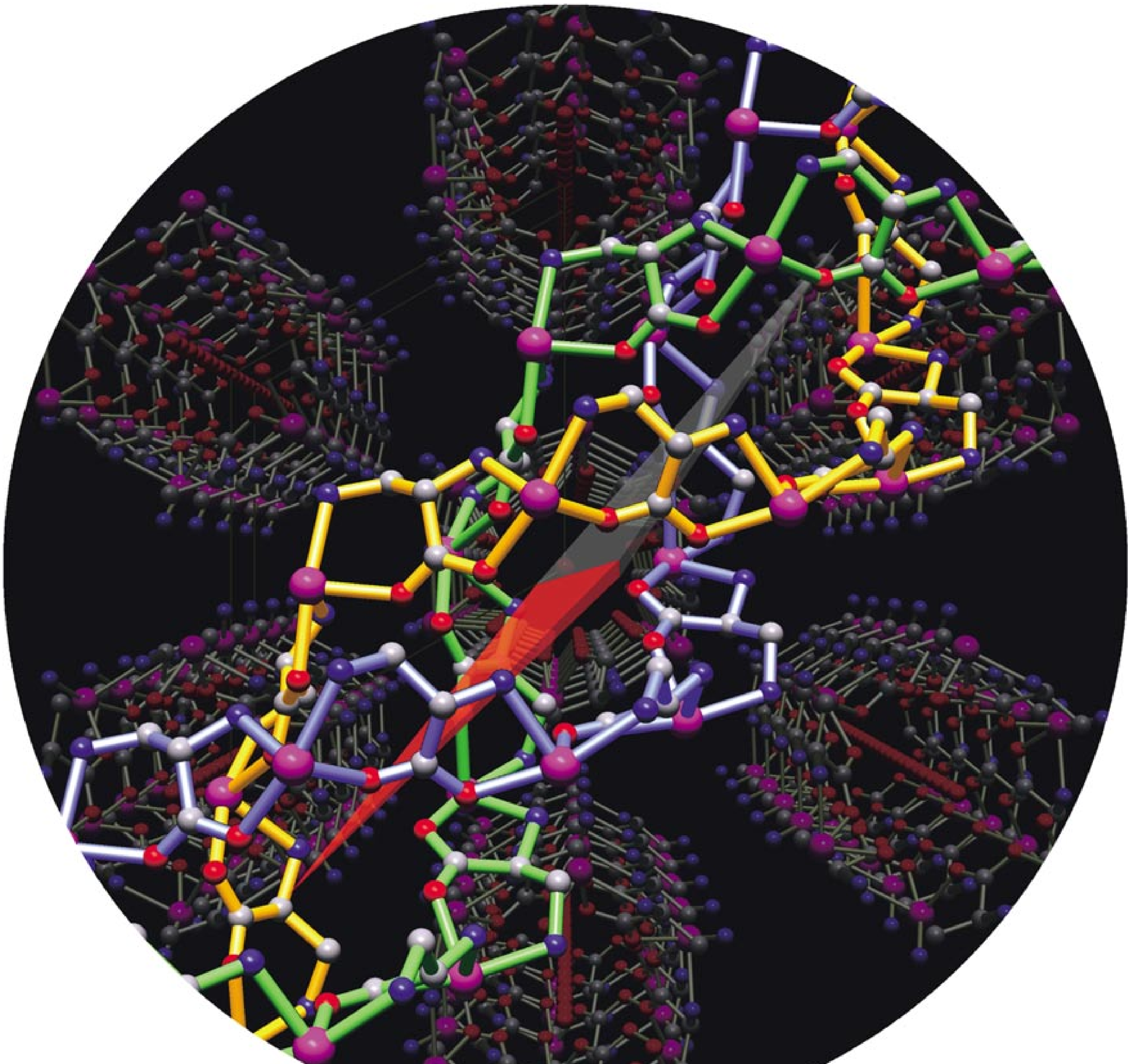
Zuschriften



Chirale tripelhelicale Stränge liegen in Kristallen der Verbindungen $[\{Cr^{III}(CN)_6\}(Mn^{II}L)_3]\cdot 3\,H_2O$ vor (L: L-NH_2ala oder L-NH_2ala; NH_2alaH = Aminoalanin). Alle Spins der Manganionen in der Anordnung zeigen unter 35 K eine ferrimagnetische Ordnung – Folge der mit den $[Cr^{III}(CN)_6]^{3-}$-Ionen gebildeten Cyanidbrücken –, die im Bild durch den roten Pfeil symbolisiert ist. Weitere Informationen zu diesen Systemen finden sich in der Zuschrift von K. Inoue et al. auf den folgenden Seiten.

DOI: 10.1002/ange.200460867

Chirality and Magnetism

Three-Dimensional Chiral Molecule-Based Ferrimagnet with Triple-Helical-Strand Structure**

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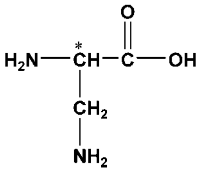
Dedicated to Professor Michinori Ōki
on occasion of his 77th birthday

In the future, development of molecule-based magnets with switching functions will lead to the production of innovative functional materials. The effect linking chirality and magnetism introduces to materials several available magneto–optical properties related to switching functions.[1,2] Most appropriate among these properties is the magneto–chiral dichroism effect (MChD). This phenomenon involves alteration of the absorbance of a substance with ordinary light according to the directions of the magnetic field and incident radiation.[1] In order to detect MChD, we have focused on the synthesis of magnetic, ordered, chiral helical compounds derived from metal complexes.

The construction of a right-handed double-helical structure within a living organism requires highly sophisticated molecular recognition, which results from the interplay of several noncovalent interactions, that is, hydrogen bonds and electrostatic and hydrophobic interactions. In the field of supramolecular chemistry, some helical complexes have been prepared.[3] The helical structures of these complexes were produced by spontaneous assemblies between suitably structured ligands and metallic ions, in which both the arrangement and the length of the helices within these complexes are programmed by the coordinating sites of the ligands and the stereochemical preferences of metallic ions. Such programs are not as accurate as those found in living organisms; consequently, extended double helical metal complexes in the solid state are rare. Therefore, to obtain magnetic ordered helical metal complexes, creation of a more accurate strategy is necessary.

Our target chiral compound with magnetic order can be synthesized by the reaction of hexacyanometalate $[M^{III}(CN)_6]^{3-}$ with a mononuclear complex $[M^{II}(L)_n]$ derived from organic chiral ligands L.[4] Generally, ligand L, which is incorporated into this system in a chelating, or bidentate fashion, to M^{II}, simply blocks the availability of some coordination sites of the M^{II} center to cyanide groups in $[M^{III}(CN)_6]^{3-}$; moreover, the ligand L does not serve as a connector between neighboring metal ions. To obtain extended helical structures of M^{II}, a novel ligand characterized by a bridging site between neighboring metals must be selected. Thus, an alanine derivative, D- or L-aminoalanine ion (D-NH_2ala or L-NH_2ala; Scheme 1), was selected as a chiral ligand molecule to meet current design requirements. This chiral organic molecule possesses two kinds of functional moieties, two amino groups and one carboxyl group, to bridge between metals. In addition, self-recognition is usually operative between the groups for assembly of amino acid molecules in crystals, in the majority of cases, through hydrogen bonds. Therefore, in this ideal case, formation of a multiple helical structure of M^{II} is expected to occur in two steps: initial construction of an infinite helical chain of ligated M^{II}, which is followed by self-assembly between the infinite chains. The hexacyanometalate $[M^{III}(CN)_6]^{3-}$ ion will connect between adjacent helical structures containing M^{II} through cyanide bridges. This linking will stabilize the structure in the solid state and to give rise to magnetic interactions through the resulting M^{III}-CN-M^{II} bridges.



$\mathrm{H_2N{-}\overset{*}{C}H(CH_2NH_2){-}C({=}O){-}OH}$

Scheme 1. Formula of D- or L- aminoalanine (D- or L-NH_2alaH).

Dark orange, hexagonal prism crystals of $[\{Cr(CN)_6\}(Mn\,L\text{-}NH_2ala)_3]\cdot 3H_2O$ (L-**1**) and $[\{Cr(CN)_6\}(Mn\,D\text{-}NH_2ala)_3]\cdot 3H_2O$ (D-**1**) suitable for X-ray analysis were obtained by slow diffusion of $MnCl_2\cdot 4H_2O$ (1.7 mmol), either D- or L-aminoalanine hydrochloride (D- or L-NH_2-alaH·HCl, 2.6 mmol), and KOH (5.2 mmol) in H_2O into $K_3[Cr(CN)_6]$ (1.5 mmol) in H_2O/*iso*-propanol (1:1) under argon atmosphere after several weeks.

X-ray crystal structure analyses at 100 K reveal that compound D-**1** crystallize in the chiral hexagonal space group, $P6_3$, and consists of left-handed helical structures of Mn^{II} ions. Compound L-**1** also crystallizes in the $P6_3$ space group but with a right-handed helical structures of Mn^{II} (Figure 1).[5] Each aminoalanine ion employs two types of functional groups to bridge between two adjacent Mn^{II} ions (Mn···Mn separation is 5.923 Å). Two amino moieties and one carboxyl group within the aminoalanine ion are coordinated to two Mn^{II} ions in terminal and bridging coordination mode,

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[**] This work is supported by a Grant-in-Aid for Scientific Research (B) (No. 15340124) from the Ministry of Education, Science, Sports, and Culture. We also thank to Professor Inabe at Hokkaido University for his advice about the crystal structure.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200460867

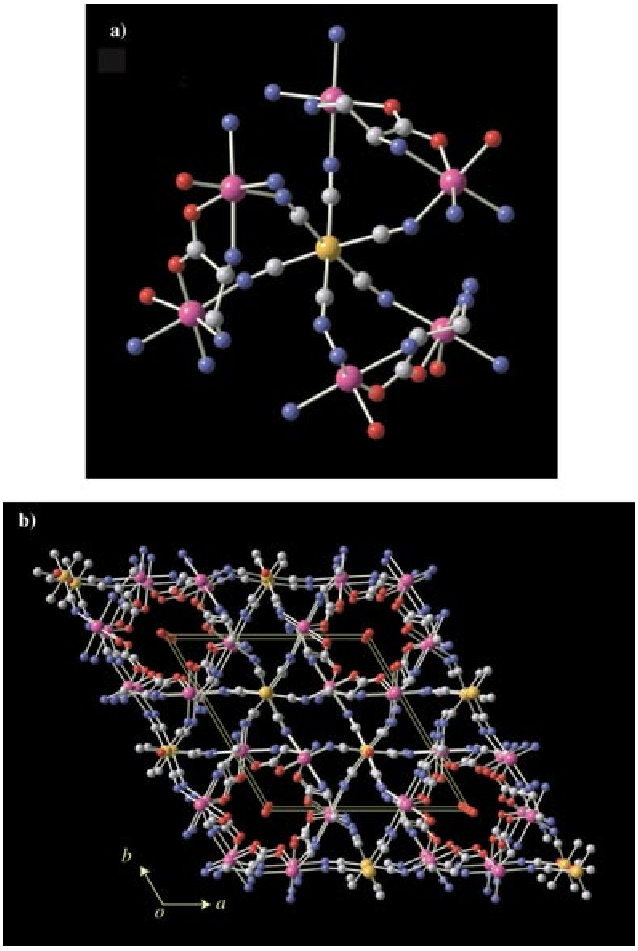

Figure 1. a) Coordination geometry of the heptanuclear unit of $[\{Cr^{III}(CN)_6\}(Mn^{II}\,\text{L-}NH_2ala)_3]\cdot 3\,H_2O$ (L-**1**). b) Overall view of the crystal structure of L-**1** along the *c*-axis. Orange Cr, purple Mn, gray C, blue N, red O. The hydrogen atoms are omitted for clarity.

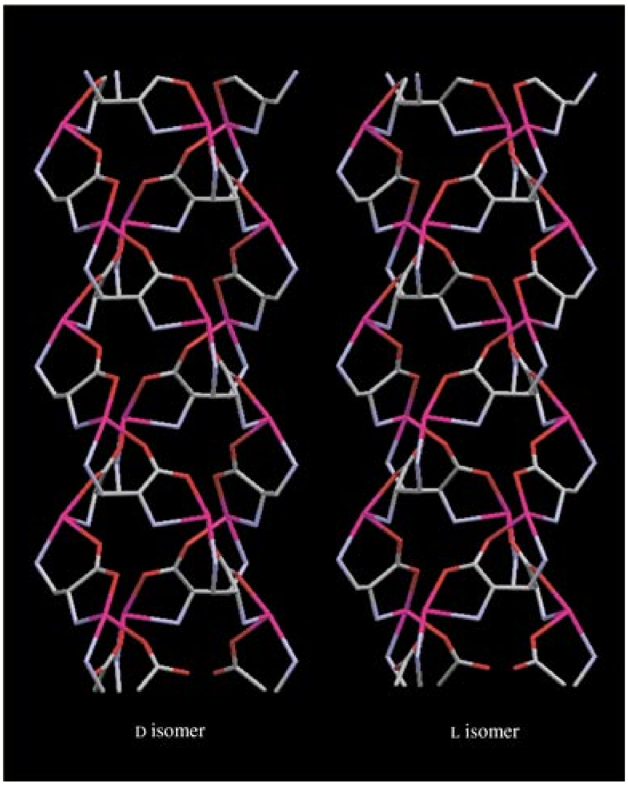

Figure 2. Capped sticks molecular models of a left-handed and a right-handed triple strand in D-**1**, and L-**1**, respectively. Purple Mn, gray C, blue N, red O.

respectively. This unique coordination leads to the construction of two differing chelating rings around the Mn^{II} ion: five- and six-membered rings. These rings align alternately resulting in the generation of extended helical chains along the *c*-axis. As expected, the helical chains link together to give aggregates of three helical chains (Figure 2), in which the shortest Mn···Mn separation between the individual chains is 6.517 Å. Within a triple helical strand, no distinct hydrogen bonds are formed between the helical chains, which usually occur between amino acid molecules. This phenomenon could be attributable to the positive charge of the manganese ions and the rigid frame of the helical chain. They maintain a distance from one another as great as 3.20 Å, which is the shortest interchain distance observed between amino nitrogen and carboxyl oxygen atoms; moreover, this distance is slightly larger than the sum of van der Waals radii. The triple helical strand structure evident in this crystal is thought to be dependent on self-recognition between helical chains. That is, a mutually complementary interaction, instead of hydrogen bonds, in which a helical pitch is united exactly, is operative between three helical chains; consequently, the triple-helical-strand structure is produced. The channel structure is generated and disordered water molecules are found in the center of the triple-helical-strand structure (on the screw axis).

Each $[Cr(CN)_6]^{3-}$ ion utilizes all its cyanide moieties to connect adjacent three triple-helical-strands through cyanide bridges to the Mn^{II} ions; as a result, a three-dimensional cyanide-bridged network is formed. The shortest and longest Cr···Mn distances through cyanide bridges are 5.490 and 5.508 Å, respectively, which are slightly longer than those in the previous crystals.[4ac]

The cyanide-bridged network also displays basic units comprised of a helical-strand structure. Each cyanide-bridged helical strand, which is composed of four metal centers (two Mn^{II} and two Cr^{III} ions) and four cyanide groups as a repeating unit characterized by a reverse turn within the helical strand of Mn^{II} and NH_2ala ions along the *c*-axis, shares the apex of the helical strand (Cr^{III} ion) between three adjacent helical strands (Figure 1).

The magnetic behavior of polycrystalline samples of compounds **1** is the same at 5000 G is illustrated in Figure 3. The $\chi_{mol}T$ value is 4.17 $cm^3\,K\,mol^{-1}$ (5.78 μ_B) at room temperature, it decreases with decreasing temperature to a minimum value of 3.91 $cm^3\,K\,mol^{-1}$ (5.59 μ_B) at 140 K. The inset in Figure 3 clarifies this behavior, in which a broad minimum peak, typical of a ferrimagnet, is observed. The $1/\chi_{mol}$ versus T plot in the range from 300 to 140 K obeys Curie–Weiss law with a Weiss temperature of $\theta = -25$ K. The negative Weiss constant indicates an antiferromagnetic interaction operates between the adjacent Cr^{3+} and Mn^{2+} ions through cyanide

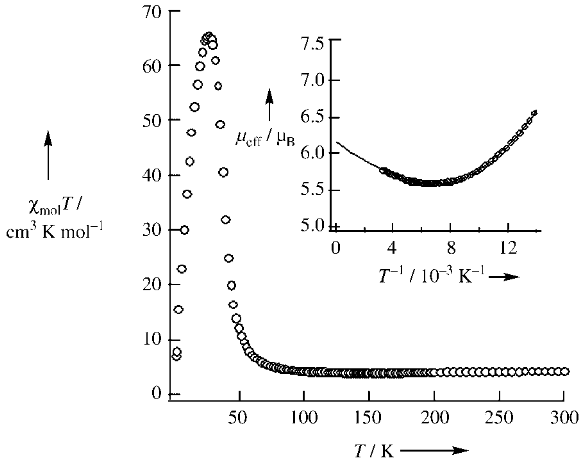

Figure 3. $\xi_{mol}T$ versus T plot at 5000 G of [{$Cr^{III}(CN)_6$}(Mn^{II} L-NH_2-ala$)_3$]·3 H_2O (L-**1**; that of D-**1** is the same). Inset: Plot of effective magnetic moment versus $1/T$.

bridges.[6] Upon additional cooling, the $\chi_{mol}T$ value increases to a maximum value of 65.38 cm^{3}K mol^{-1} (22.87 μ_B) at 27 K, followed by subsequent decreases below this temperature. The abrupt increase of the $\chi_{mol}T$ value around 30 K suggests the onset of three-dimensional magnetic ordering. The extrapolated effective magnetic moment value is 6.16 μ_B, which corresponds to the theoretical spin-only value of noncoupled paramagnetic high spin in the high-temperature limit (Figure 3 inset).

Low-field magnetization measurements of polycrystalline samples of compounds **1** at an applied field of 5 G in the temperature range 1.8–100 K were performed to confirm long-range magnetic ordering around 35 K (Figure 4). Both the zero field-cooled magnetization (ZFCM) and field-cooled magnetization (FCM) curves demonstrate long-range magnetic ordering below 35 K (Figure 4). As shown in the inset of Figure 4, the magnetization versus field (***M*** vs ***H***) plot of polycrystalline samples at 2 K increases sharply with the applied field and is saturated rapidly. The saturation magnetization is $M_S = 3.93\ \mu_B$; this value is consistent with the theoretical value of antiferromagnetic coupling between one Mn^{2+} and one-third of a Cr^{3+} ion (5/2−1/2 = 4/2).

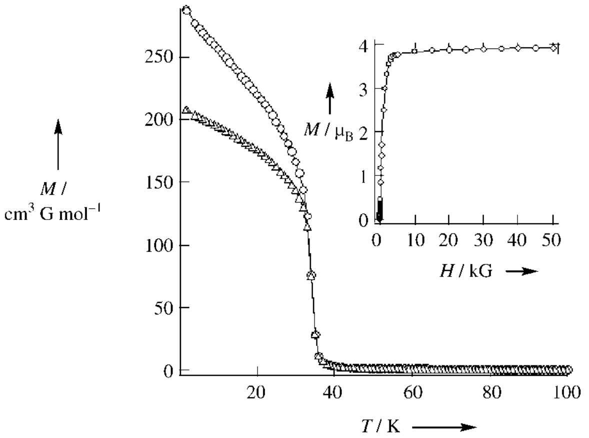

Figure 4. Temperature dependence of magnetization of L-**1**. The FC (△) and ZFC (○) magnetizations at 5 G are shown. Inset: Field dependence of magnetization L-**1** at 2 K. The results for D-**1** are the same.

In conclusion, the results demonstrate that a compound with a triple-helical-strand structure is synthesized from the reaction of manganese(II) complex with an alanine derivative and hexacyanochromate(III) ion. These compounds, which have a triple-helical structure with counterclockwise and clockwise turns around the manganese ion, were obtained from D and L isomers, respectively. Detailed analysis of crystal structure also indicates that the main factor governing this phenomenon is not hydrogen bonding between helical chains, as expected, but the rigid frame of the helical chain. Owing to the rigid frame and positive charge of the helical chain, the helical chains cannot approach one another sufficiently closely in the crystal to permit interchain hydrogen-bond formation; thus, the rigid frame is advantageous with respect to triple-helical-strand formation.

The compounds exhibits ferrimagnetic behavior below 35 K. The magnetic transition temperature of both compounds is relatively low despite formation of a three-dimensional cyanide network. This phenomenon is probably attributable to the comparatively long cyanide-bridged distance in this crystal. In addition, it may result from the occurrence of spin frustration between manganese ions within the triple-helical strand at high temperature. Below 35 K, the spin on the manganese center alone survives owing to the ferrimagnetic coupling between manganese and chromium ions. The spin structure of this compound is also expected to possess triple-helical nature. Some chiral molecule-based magnets have been prepared, however, at present, a chiral helical spin structure has not been documented. Magnetization measurements, μSR (muon spin resonance) spectroscopy and neutron diffraction of a single crystal will lead to characterization of the details of the magnetic structure in this compound.

Received: June 4, 2004
Published Online: September 28, 2004

Keywords: chirality · chromium · helical structures · magnetic properties · manganese

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[5] Crystal data for L-isomer (L-**1**): Crystal size $0.35 \times 0.35 \times 0.20\ \text{mm}^3$. $C_5H_9Cr_{0.33}MnN_4O_3$, $M_r = 245.44$, hexagonal, $P6_3$ (No. 173), $a = b = 13.6802(16)$, $c = 8.1530(14)$ Å, $V = 1321.4(3)$ Å^3, $T = 100$ K, $Z = 6$, $\rho_{calcd} = 1.851\ \text{g cm}^{-3}$, $\mu(\text{Mo}_{K\alpha}) = 1.870\ \text{mm}^{-1}$. Data were collected with a Bruker SMART-APEX three-circle diffractometer, equipped with a CCD area detector (graphite-monochromated $\text{Mo}_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, ω-scan mode (0.3° steps), semi-empirical absorption correction on Laue equivalents). The structures were solved by direct method and refined by full-matrix least squares against F^2 of all data, using SHELXTL software. All-non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except for the water hydrogen atoms, were placed in calculated positions but not refined. The refinement converges with $R_1 = 0.0440$ for 1192 data ($I > 2\sigma(I)$), $wR_2 = 0.1169$ for 1194 unique data ($1.72 \geq \theta \geq 23.24°$), Flack parameter $= 0.05(6)$, max/min residual electron density $0.566/-0.608\ \text{e Å}^3$. CCDC-238055 (L-**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[6] See Supporting Information.