

Transformation of Cadmium Tetracyanoquinodimethane (TCNQ) into a Cadmium Terephthalate Metal–Organic Framework

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The transformation of cadmium 7,7,8,8-tetracyanoquinodimethane (TCNQ) into a cadmium terephthalate co-ordination polymer is reported, with the chemistry of this material elucidated using elemental analysis, X-ray photoelectron spectroscopy and synchrotron radiation single-crystal X-ray diffraction. A heptacoordinated Cd^{II} linear coordination polymer *catena*-poly[triaqua-(μ₂-benzene-1,4-dicarboxylato-κO,O')cadmium(II)]hydrate (**1**) was isolated while attempting to recrystallize Cd(TCNQ)₂. Density functional theory calculations for the oxidation of benzylic carbon attached to the cyano group provided evidence that the reaction pathway proposed herein is highly exergonic and thermodynamically plausible. This structure showed a distorted pentagonal bipyramidal geometry together with a symmetrical mononuclear unit in which each Cd^{II} ion is doubly bridged by a dicarboxylato anion. Owing to the softness and minute size of these crystals, this structure had to be elucidated using synchrotron radiation X-ray crystallography.

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Introduction

The coordination chemistry of cadmium is of significant interest owing to the impact of its mobility in environmental and biological systems.^[1] Coordination polymers of cadmium with uni- or multidimensional topologies have also found extensive use in the fields of gas occlusion, catalysis, ion-exchange, magnetism, molecular recognition, photoluminescence, and laser applications.^[2] The reduced anion radical of 7,7,8,8-tetracyanoquinodimethane (TCNQ^{•-}), which is of interest in the present study, has been widely used as a strong electron acceptor and forms highly conductive charge-transfer complexes.^[3] Research on transition metal coordination polymers of TCNQ^{•-} is also driven by their potential applications in optical and electrical recording media, energy, and data storage, as well as electrochromic and magnetic devices.^[4] In this context, it is

important to understand the long-term stability of TCNQ^{•-} materials. For example, the TCNQ^{•-} anion radical can hydrolyze to aromatic dicarboxylate ligands, which in turn are interesting as they are excellent candidates for producing highly porous metal–organic composite materials and provide rigid-rod conjugated bones or linkers with regularly spaced inorganic centres.^[5]

Recently, the authors have been interested in the electrocrystallization of Cd–TCNQ materials and their structural characterization. Here, we report on the transformation of Cd(TCNQ)₂ into a hitherto unreported heptacoordinated Cd^{II} one-dimensional coordination polymer with 1,4-dicarboxylate benzene ligands, resulting from the slow oxidation of benzylic carbons in TCNQ^{•-} that occurred during attempts to grow microcrystals from tetrahydrofuran (THF) solutions of Cd

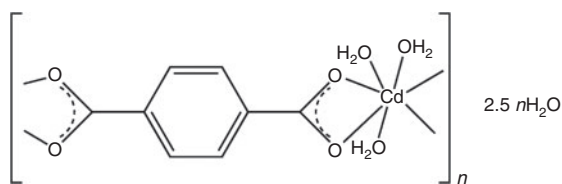


Chart 1. Structural representation of **1**, $C_8H_{15}CdO_{9.50}$.

(TCNQ)₂ that were suitable for structural analysis by synchrotron radiation (SR) X-ray crystallography. The stoichiometry of **1** (see Chart 1) is confirmed by elemental analysis and X-ray photoelectron spectroscopy (XPS). A plausible reaction pathway is proposed that is based on density functional theory (DFT) calculations of hydrolyzed and oxidized TCNQ ligand pathways as observed experimentally by Cehak et al.^[5c]

Results and Discussion

X-Ray Structure

The crystal structure of **1**, as determined by SR X-ray crystallography, is shown in Fig. 1 with the unit cell presented in Fig. 2. The structure consists of two μ_2 -benzene-1,4-dicarboxylato ligands, both situated on crystallographic inversion centres, bridging between two metal centres forming a one-dimensional linear polymer. Each Cd^{II} ion is bonded to four oxygen atoms from the two ligands and to three oxygen atoms from coordinated water molecules. There are also three solvent water molecules per Cd^{II} ion, one of which is disordered over four sites around a crystallographic inversion centre. The Cd^{II} coordination sphere is best described as a distorted pentagonal bipyramidal system with the base consisting of four carboxylate oxygen atoms plus one water molecule, with the remaining water molecules (two) occupying the apical positions.

The angles subtended at the Cd^{II} centre by adjacent equatorial O atoms are larger (82.8(2)–86.2(2)°) than the ideal value of 72° for a bipyramidal structure, while the two angles involving four-membered metal carboxylate rings are expectedly smaller (54.2)–54.4(2)°.^[6] The angle between the two water molecules present at the apical positions also show a deviation (O(1)–Cd–O(2) = 169.9(2)°) from the ideal value of 180°. This might be due to a bent structure for the water molecules.^[7] The distortion from a perfect bipyramidal structure is also observed in the angles between the axial and equatorial bonds, which range from 80.4(2)° to 100.7(2)°. The equatorial Cd–O bonds (2.329(4)–2.481(6) Å) are longer than those of apical water molecules (Cd(1)–O(1), O(2) 2.285 and 2.286(6) Å). This is in accordance with related structures that have been reported previously.^[8] Among the equatorial Cd–O bond lengths of the bridging ligands are Cd(1)–O(12) and Cd(1)–O(21) that are in close proximity, as are the Cd(1)–O(22) and Cd(1)–O(11) ones. Finally, Fig. 2 shows that the polymers are packed in sheets in the unit cell parallel to the *ac* plane that are at approximately *y* = 0 and 1.0 with parallel sheets of water molecules at *y* = 0.5.

Elemental Analysis

Cd(TCNQ)₂ was synthesized and characterized electrochemically as described elsewhere.^[9] Elemental analysis of freshly prepared material showed the presence of nitrogen, carbon, and cadmium at close to the theoretically expected values for the synthesis of Cd(TCNQ)₂ (theoretical values of 55.3 % C, 1.55 % H, 21.5 % N, 21.6 % Cd, and 0 % O versus experimental ones of 55.7 % C, 1.58 % H, 20.7 % N, 22.1 % Cd, and 0.1 % O).

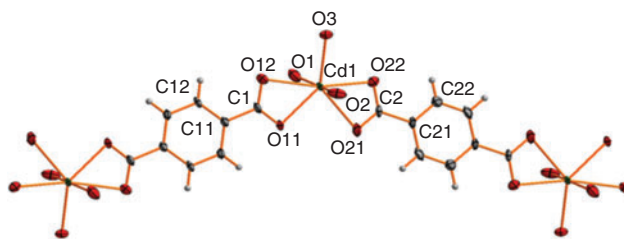


Fig. 1. Representation of the structure showing the polymeric nature of $C_8H_{15}CdO_{9.50}$.

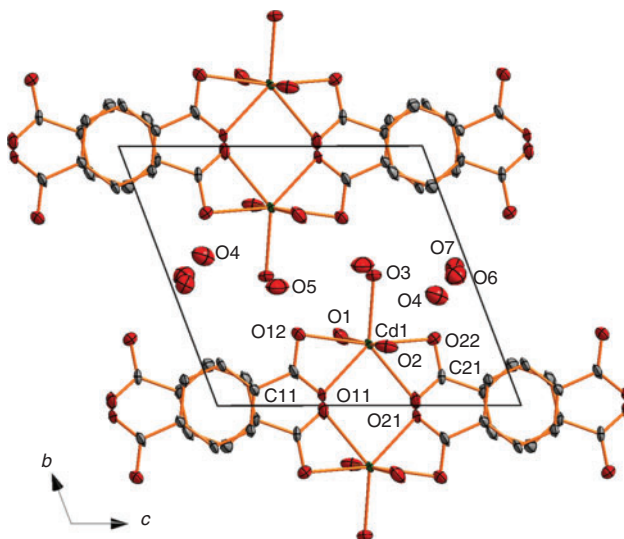


Fig. 2. Unit cell of $C_8H_{15}CdO_{9.50}$ projected along the *a* axis.

The small quantity of oxygen can be attributed to the presence of a trace of H₂O. However, after the attempted slow recrystallization of Cd(TCNQ)₂ from THF, elemental analysis showed that nitrogen was completely absent and oxygen was present in a high proportion. Calculated and expected compositions matched the chemical formula given for **1** in Chart 1 as derived from X-ray crystallography (theoretical values of 25.6 % C, 4 % H, 0 % N, 29.9 % Cd, and 40.5 % O versus experimental ones of 24.7 % C, 4.5 % H, 0 % N, 28.8 % Cd, and 42.1 % O).

XPS Analysis

XPS was used to determine the binding energies of Cd, N, O, and C core levels for freshly synthesized Cd(TCNQ)₂ and recrystallized material. It is evident in Fig. 3 that there is a characteristic N 1s peak at 398.9 eV together with Cd 3d_{5/2} and Cd 3d_{3/2} peaks at 405.0 and 411.9 eV that are indicative of CN and Cd^{II} in Cd(TCNQ)₂ respectively. However, after the attempted recrystallization in THF, the N 1s peak from TCNQ[−] is absent, demonstrating that decomposition of the Cd(TCNQ)₂ has occurred. By contrast, although there is an insignificant O 1s peak in freshly synthesized Cd(TCNQ)₂ (not shown), two forms of oxygen at binding energies of 530.9 and 532.1 eV are evident in the decomposed material. The sharp peak at 530.9 eV with a full-width at half-maximum (FWHM) of 1.25 eV is attributable to COO[−] oxygen in the dicarboxylato ligand, whereas the broad peak at 532.1 eV with FWHM of 2.0 eV is ascribable to oxygen in hydrogen-bonded water that is coordinated to the Cd^{II} bonding centre.^[10] Notably, the O 1s peak area ratio for COO[−] to H₂O is close to 4 : 3, as expected for the structure depicted in

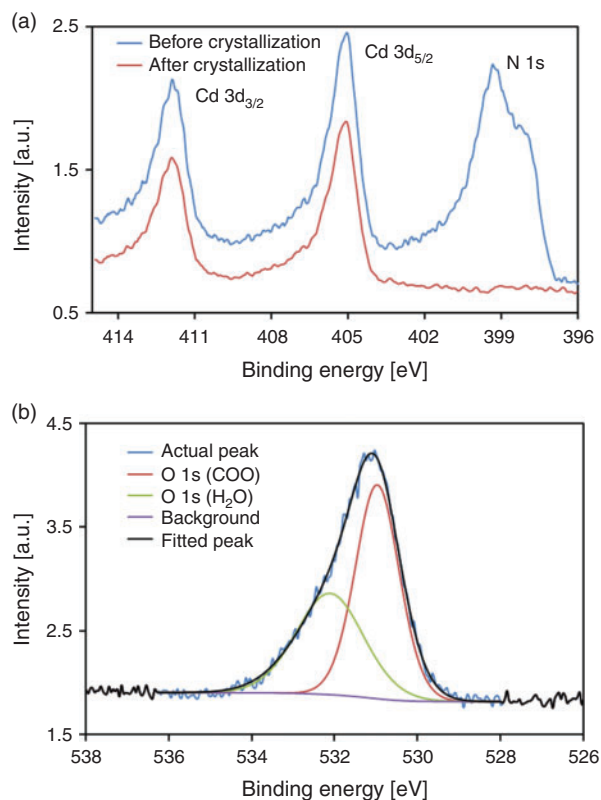


Fig. 3. (a) N 1s and Cd 3d core-level XPS spectra of Cd(TCNQ)₂ before and after the attempted recrystallization; and (b) O 1s core-level XPS spectra of compound **1**.

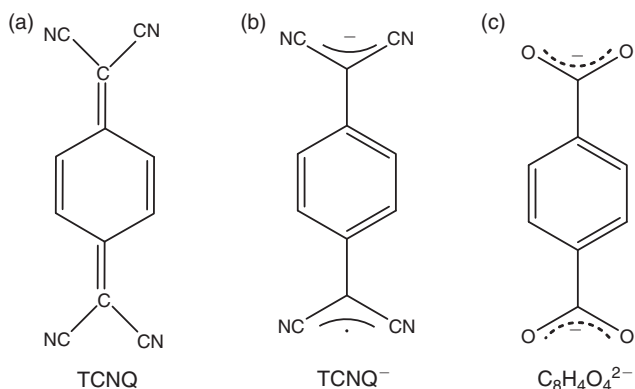


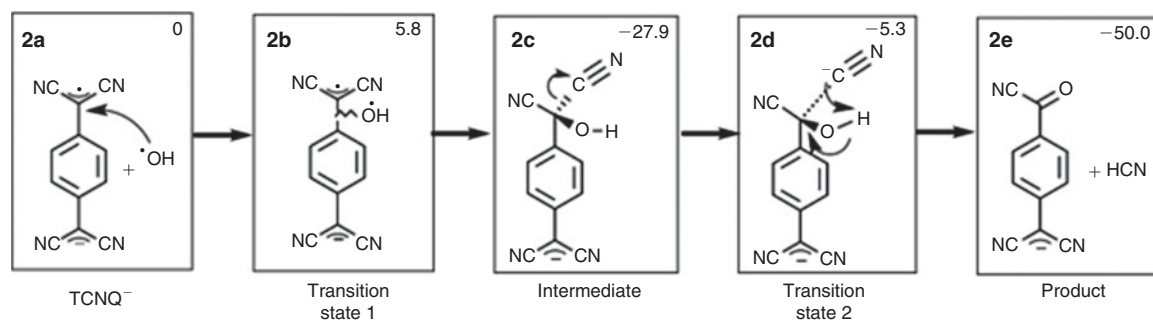
Chart 2. Structures of (a) TCNQ; (b) TCNQ⁻; and (c) C₈H₄O₄²⁻.

Chart 1 without the waters of hydration. It is highly probable that the waters of crystallization have volatilized under the ultrahigh vacuum conditions of the XPS analyser chamber, so have evaded detection by XPS. Finally, the presence of a C 1s shoulder at ~289 eV (not shown) is also indicative of COO⁻ in the dicarboxylate ligand.

Proposed Mechanism for TCNQ Oxidation – DFT Calculations

It is well known that benzylic carbon is prone to oxidation by atmospheric oxygen in the presence of UV-visible light.^[11] TCNQ (**Chart 2a**) contains two benzylic carbons present in both the *para* and *trans* configurations. In addition to the benzene ring, each of these benzylic carbons is attached to two strongly electron-withdrawing cyano groups, making them even more reactive.^[12] Coordination of the reduced TCNQ ligand (**Chart 2b**) with the metal ion further weakens the C–C bond, such that these moieties in a TCNQ metal derivative might be sensitive to oxidation by atmospheric oxygen. Consequently, in a reaction mixture comprising benzylic carbons that may react with atmospheric oxygen, water or light, it is plausible to expect oxidation of these benzylic carbons into carboxylate groups, resulting in a transformation of TCNQ⁻ into a 1,4-benzenediacarboxylate (**Chart 2c**) ligand.

DFT calculations were carried out to interrogate theoretically the possibility of oxidation of benzylic carbon in TCNQ⁻. To make the DFT calculations less computationally intensive, yet representative of a possible reaction pathway, an [•]OH radical was used to oxidize the benzylic carbon in a reaction that replaces a CN group with C=O, as illustrated in **Scheme 1**. Optimized geometries of all stationary points are shown in **Fig. 4**. The reactant **2a** (**Scheme 1** and **Fig. 4**) consists of TCNQ⁻ and the [•]OH radical. The transition state structure **2b** (relative energy +5.8 kcal mol⁻¹; 1 kcal mol⁻¹ = 4.186 kJ mol⁻¹) corresponds to the attack of the [•]OH radical onto TCNQ⁻, where the OH group is directly interacting with two carbon atoms of TCNQ⁻. The next step is the formation of intermediate **2c** (relative energy –27.9 kcal mol⁻¹), in which both OH and leaving CN groups are covalently bonded to the benzylic carbon. Normal mode analysis shows that structure **2d** (relative energy –5.3 kcal mol⁻¹) is a transition state for HCN release. The last structure of the energy profile, **2e**, is –50.0 kcal mol⁻¹ more stable than **2a**. Consequently, the replacement of CN with O involves the highest energy barrier of +5.8 kcal mol⁻¹ (transition state **2b**) and is a highly exothermic reaction (ΔH –50.0 kcal mol⁻¹). We also calculated the reaction energies for replacement of the second, third, and fourth CN groups of TCNQ⁻. The computed energy



Scheme 1. Replacement of a CN group in TCNQ⁻. Energy values (kcal mol⁻¹) at the top right of each panel for structures **2a** to **2e** are relative to the reactant **2a**.

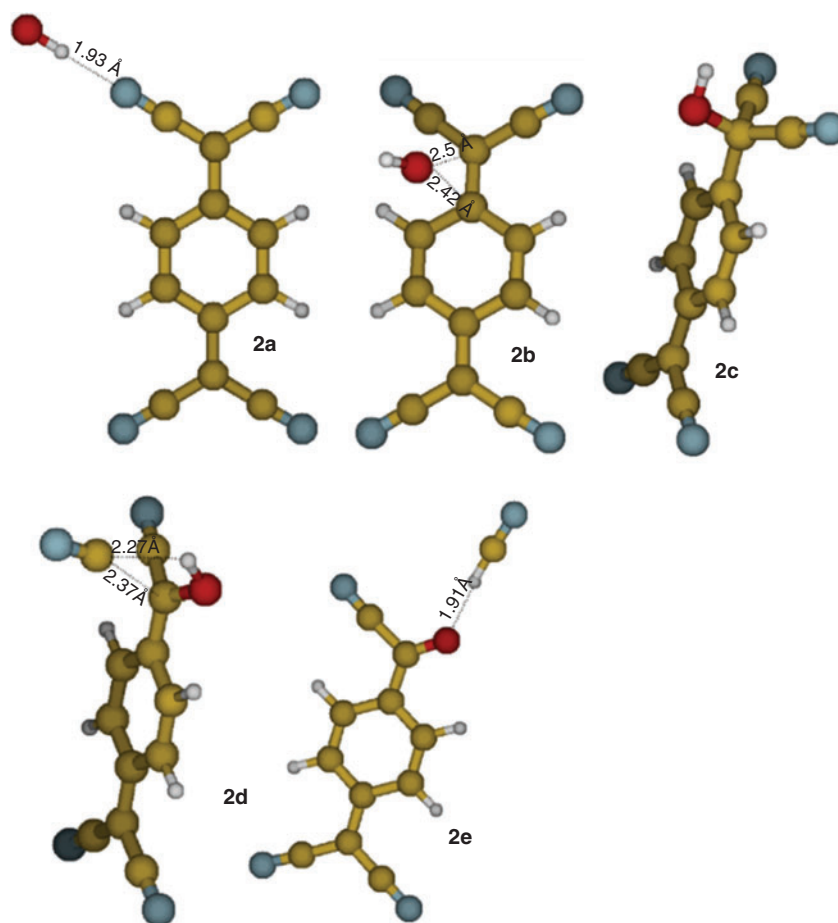


Fig. 4. Optimized geometries of the stationary points, at the B3LYP/6-31+G(d,p) level for the first CN replacement displayed in Scheme 1.

values at the B3LYP/6-31G(d) level are -38.0 , -66.4 , and $-38.9 \text{ kcal mol}^{-1}$ respectively. This indicates that replacement of each CN group is highly exothermic. Given that the metal coordination and entropic effects in hydrated $\text{Cd}(\text{TCNQ})_2$ are anticipated to be approximately the same as those in the hepta-coordinated Cd^{II} linear coordination polymer *catena*-poly[triaqua- $(\mu_2$ -benzene-1,4-dicarboxylato- $\kappa\text{O},\text{O}'$)cadmium(II)]hydrate (**1**), this reaction is expected to be strongly exergonic (viz. a high negative value for ΔG where $\Delta G = \Delta H - T\Delta S$) and hence thermodynamically plausible and possible.

Conclusions

In this paper, it is demonstrated that a room-temperature transformation of the cadmium tetracyanoquinodimethane complex into a cadmium terephthalate complex occurs via slow aerial oxidation of cyano functionalities within the TCNQ^- ligand. The structure of the cadmium terephthalate coordination framework has been elucidated using SR X-ray crystallography and confirmed by elemental analysis and XPS. A plausible reaction mechanism is proposed on the basis of DFT theoretical calculations.

Experimental

Materials and Methods

Cadmium nitrate tetrahydrate, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, TCNQ, tetrabutylammonium perchlorate (TBAP), acetonitrile, THF, and

methanol were purchased from Sigma–Aldrich in the highest purity available. Acetonitrile and THF were distilled before use. The synthesis of $\text{Cd}(\text{TCNQ})_2$ was carried out electrochemically using an Autolab PGSTAT128N (Metrohm Autolab, Utrecht, The Netherlands) workstation using a procedure based on a previously published method.^[4,9,13] A standard three-electrode cell was used with a high-surface-area (265 mm^2) gold working electrode, a platinum mesh counter-electrode and an Ag/AgCl/saturated KCl/1 M LiOAc double-junction reference electrode (Mettler-Toledo AG, Schwerzenbach, Switzerland). TCNQ was reduced to TCNQ^- by applying a constant potential of -0.5 V in acetonitrile solution also containing 0.1 M TBAP and 0.1 M $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, which resulted in the deposition of $\text{Cd}(\text{TCNQ})_2$ on the gold electrode surface.

The XPS analyses were performed on a Kratos AXIS Ultra instrument using a monochromatic Al $K\alpha$ X-ray source (1486.6 eV) at 150 W. Elemental analysis (CHNO) was carried out using the PerkinElmer 2400 elemental analyser fitted with an oxygen accessory kit.

Crystals of **1** were obtained during the course of the attempted recrystallization of $\text{Cd}(\text{TCNQ})_2$ in THF via a slow evaporation method over a period of 2 months. However, this produced light-yellow block-like crystals with the empirical formula of $\text{C}_8\text{H}_{15}\text{CdO}_{9.50}$ instead of the expected $\text{Cd}(\text{TCNQ})_2$. Owing to the micrometre size and soft nature of these crystals, it was essential to elucidate their structure by SR X-ray microcrystallography.

Table 1. Crystal data and structure refinement for **1**

| 1 | |
|---|--|
| Empirical formula | C ₈ H ₁₅ CdO _{9.50} |
| Formula weight | 375.60 |
| Temperature | 100(2) K |
| Wavelength | 0.71252 Å |
| Crystal system | Triclinic |
| Space group | <i>P</i> $\bar{1}$ |
| Unit cell dimensions | <i>a</i> = 7.0630(10) Å <i>b</i> = 9.7000(10) Å <i>c</i> = 10.1060(10) Å α = 108.771(2)° β = 92.874(2)° γ = 107.702(2)° |
| Volume | 616.04(12) Å ³ |
| Z | 2 |
| Reflections collected | 6343 |
| Independent reflections | 3347 [<i>R</i> (int) = 0.0689] |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | <i>R</i> ₁ = 0.0652, <i>wR</i> ₂ = 0.1611 |
| <i>R</i> indices (all data) | <i>R</i> ₁ = 0.0872, <i>wR</i> ₂ = 0.1800 |

DFT calculations for the oxidation of benzylic carbons attached to CN groups in TCNQ[−] were carried out using the •OH radical (Scheme 1 and Fig. 4). Structures were optimized using the B3LYP hybrid functional^[14] together with the 6-31+G(d) basis set. Single-point energies were calculated at the B3LYP/6-311++G(d,p) level of theory. Energy values listed in Scheme 1 are B3LYP/6-311++G(d,p)/B3LYP/6-31+G(d)+ZPE energies relative to the reactant **2a**, where ZPE stands for zero-point energy. Energy minima and first-order saddle points were confirmed by the frequency calculations at B3LYP/6-31+G(d) level. All calculations were performed using the *Gaussian 09* program.^[15]

Crystallographic Data Collection and Structure Determination

The experimental parameters for crystal data collection are summarized in Table 1, with the structure of **1** depicted in Figs 1 and 2, where the ellipsoids have been drawn at the 70% probability level. Crystal data and structure refinements together with selected bond lengths and angles are presented in Tables S1 and S2 (Supplementary Material) respectively. Diffraction data were collected at 100 K on beamline MX2 at the Australian Synchrotron ($\lambda = 0.71252$ Å). Following solution by direct methods, the structure was refined against *F*² with full-matrix least-squares using the program *SHELXL-97*.^[16] One water molecule was modelled as disordered about a crystallographic inversion centre with site occupancies of each site constrained to 0.25. All non-hydrogen atoms were refined with anisotropic displacement parameters. Water molecule hydrogen atoms could not be located. All remaining hydrogen atoms were added at calculated positions and refined by using a riding model with isotropic displacement parameters based on those of the parent atoms.

The CIF file containing lists of all of the bond lengths and angles is available through the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, on quoting the reference number CCDC 100836.

Supplementary Material

Crystal data and structural refinements together with selected bond lengths (Å) and angles (°) for C₈H₁₅CdO_{9.50} (Tables S1

and S2 respectively) as well as Cartesian coordinates of the optimized geometries at the B3LYP/6-31+G(d,p) level (Appendix S1) are available on the Journal's website.

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