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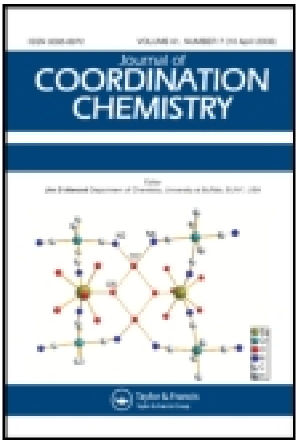

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8-Aminoquinoline as a new bidentate ligand for *cis*-MoO_2: synthesis and characterization of a dioxomolybdenum(VI) amide $[MoO_2(NHC_9H_6N)_2]$

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The reaction of $(Bu_4N)_2[Mo_6O_{19}]$ with 8-aminoquinoline in the presence of DCC (*N,N*′-dicyclohexylcarbodiimide) afforded the *cis*-dioxo-Mo(VI) amide $[MoO_2(NHC_9H_6N)_2]$, which was characterized by spectroscopy, mass spectrometry, ^{1}H NMR, and single-crystal X-ray analysis. X-ray crystallography shows that the complex exhibits a distorted octahedral geometry with each oxo ligand *trans* to the quinolyl nitrogen and the amido ligands are bound to the metal in an *N,N*-chelating fashion. The molecules form zigzag chains *via* C–H$\cdots$O hydrogen bonds and the chains are connected into networks through interchain N–H$\cdots$O hydrogen bonds.

Keywords: Dioxomolybdenum(VI); Aminoquinoline; Amide; Complex; Crystal structure

1. Introduction

The study of oxo-molybdenum complexes has received increasing attention for important roles in various biological and industrial oxidation processes [1–3]. In particular, a variety of molybdenum complexes containing the dioxomolybdenum(VI) core, MoO_2^{2+}, have been studied, especially as structural and functional biomimetic models for the active sites of oxo transfer molybdoenzymes in biological catalytic oxidation reactions [4–7]. In addition, dioxomolybdenum complexes are also employed in many artificial oxidations [8], including isomerization of allyl alcohols, olefin epoxidation, and oxidation of propene in the SOHIO process [9–11].

Dioxomolybdenum(VI) coordinates to a wide range of ligands to form $Mo(VI)O_2L_n$ with L mono-, bi-, tri-, or tetradentate. Such complexes possess the following general formulae: $[MoO_2X_2(L^1)_n]$, $[MoO_2(L^2)(L^1)_n]$, and $[MoO_2(L^2)_2(L^1)_n]$ (X = Cl, Br, CH_3, OR etc., L = mono or bidentate neutral (L^1) or anionic (L^2) ligands with nitrogen, oxygen/sulfur donors) [12–16]. However, the chemistry of dioxomolybdenum(VI) complexes with amido derivatives remains relatively little studied. Especially, a combination of dioxidomolybdenum(VI) with quinoline-functionalized amido ligands has never been reported.

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Coordination chemistry of 8-aminoquinoline has attracted much interest [17–19] because it can ligate to metal centers in a variety of binding modes as monodentate amide, bidentate *N,N*-bridge, and *N,N*-chelate. A number of transition metal complexes containing 8-aminoquinoline have been synthesized and structurally characterized. 8-Aminoquinoline is a relatively bulky planar ligand, which facilitates the formation of mononuclear metal complexes and prevents association to form bi- and multinuclear complexes. In this article, we report a new mononuclear *cis*-dioxo-Mo(VI) complex containing two 8-aminoquinoline ligands. Other than synthesizing dioxomolybdenum complexes using reagents containing MoO_2^{2+}, such as $[MoO_2(acac)_2]$ and $[MoO_2Cl_2(DME)]$ (DME = 1,2-dimethoxyethane) [20–23], we found a new reaction of $(Bu_4N)_2[Mo_6O_{19}]$ with 8-aminoquinoline in the presence of DCC that afforded the dioxo-Mo(VI) complex $[MoO_2(NH\text{-}C_9H_6N)_2]$. The reaction presents another route employing polymolybdate clusters as Mo-releasing reagents to synthesize such complexes. Owing to the important roles of dioxomolybdenum complexes in biological and industrial oxidations, the prepared complex provides an opportunity to explore its application in such processes for the investigation on the mechanisms of these oxidations.

2. Experimental

2.1. *General considerations*

8-Aminoquinoline, DCC, diethyl ether, and DMF were used as received. Acetonitrile was dried by refluxing in the presence of CaH_2 and was distilled prior to use. $(Bu_4N)_2[Mo_6O_{19}]$ was synthesized according to an improved literature method [24] and was recrystallized from anhydrous acetone and dried before use. 8-Aminoquinoline was also dried before use. UV-Vis absorption spectrum was recorded in DMF with a TU-1810 spectrophotometer. IR spectrum was recorded in KBr pellets with a Bruker Equinox 55 spectrophotometer. ^1H NMR spectrum was taken on a Bruker Avance 300 NMR spectrometer at 298 K using DMSO-d_6 as the solvent. The mass spectrum was recorded using an AB Sciex 4000 Q TRAP spectrometer. Elemental analysis was performed on a Perkin Elmer 2400 series II CHNS/O analyzer. A suitable single-crystal having approximate dimensions of $0.49 \times 0.19 \times 0.07\,mm^3$ was mounted on a glass fiber. The measurements were made on a Bruker SMART APEX II diffractometer. The data collection was performed at 293 K with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. The structure was solved by direct methods and refinement was performed by full-matrix least-squares on F^2 with SHELXTL-97 [25]. All of the nonhydrogen atoms were refined anisotropically and hydrogens were included at their idealized positions.

2.2. *Preparation of the complex*

A mixture of 8-aminoquinoline (1.0 mmol, 0.144 g), DCC (1.3 mmol, 0.270 g), and $(Bu_4N)_2[Mo_6O_{19}]$ (1.0 mmol, 1.37 g) was refluxed in anhydrous acetonitrile (15 mL) for about 23 h. The reaction mixture dissolved completely in anhydrous acetonitrile with the increase in temperature and the solution turned red. During the course of the reaction, the color changed to red-brown, and red precipitates formed. When the resulting solution was cooled to room temperature, the red precipitates were collected by filtration and dissolved in DMF. Then red single crystals of the complex (yield: 0.51 g, 22.3%) were obtained by slow diffusion of diethyl ether into the solution in DMF.

2.3. *Characterization of the complex*

Elemental Anal. Calcd for $MoO_2C_{18}N_4H_{14}$ (%): C 52.19, H 3.41, N 13.52; Found (%): C 51.89, H 3.63, N 13.34. ^{1}H NMR (300 MHz, DMSO, 298 K): δ 9.55(s, 2H, –NH), 8.60(d, 2H, quinoline), 8.25(d, 2H, quinoline), 7.40(m, 4H, quinoline), 7.05(m, 4H, quinoline). UV-Vis (DMF, nm): $\lambda = 270$, 344, and 445. IR (KBr pellet, major absorbances, cm^{-1}): 3340, 3040, 1573, 1506, 1470, 1340, 912, 870. EI-MS (70 eV): $m/z = 417.0$ (M^+).

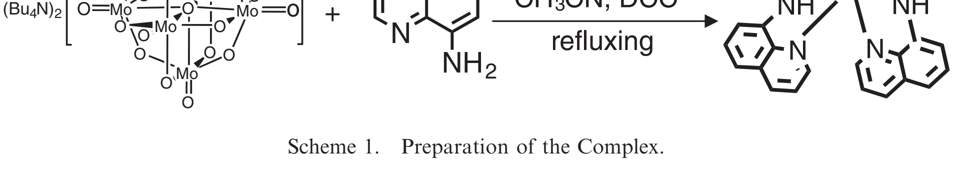
3. Results and discussion

3.1. *Preparation of the complex*

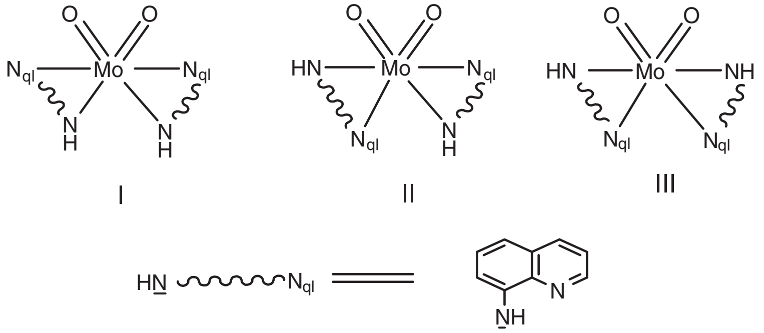
The reaction of 8-aminoquinoline with $(Bu_4N)_2[Mo_6O_{19}]$ in the presence of DCC (*N,N′*-dicyclohexylcarbodiimide) refluxing in anhydrous acetonitrile affords the mononuclear *cis*-dioxo-Mo(VI) amido complex in satisfactory yields (scheme 1). The reaction was designed to prepare the quinolylimido derivative of hexamolybdates according to the DCC protocol [26]. However, a new *cis*-dioxomolybdenum amido complex with 8-amimoquinoline as bidentate ligands is unexpectedly obtained. The crystals are red and readily soluble in strongly polar organic solvents such as DMF and DMSO, while sparingly soluble in common polar solvents such as acetonitrile and acetone.

Similar to reported dioxo-molybdenum amides containing pyridine-functionalized [27] amido ligands, three configurational isomers would be expected for this type of *cis*-dioxo complex (scheme 2). According to the molecular structure of the complex confirmed by single-crystal X-ray analysis, only configurational isomer III, with oxygen *trans* to the quinoline nitrogen, was isolated. This may be attributed to strong *trans* influence of the oxo ligands which renders the formation of configurational isomers I and II unfavorable.

Since the cluster skeleton changed during the reaction, cluster disassembly must be involved in the reaction process. Polymolybdate clusters are easy to disassemble under certain conditions [28]. It is likely that the hexamolybdate ion is first decomposed to $[MoO_4]^{2-}$. The amido group of 8-aminoquinoline may be deprotonated by oxide, probably from molybdate, to form H_2O, which is then removed by the dehydrating agent DCC. Thus, a nucleophilic intermediate $[^-NHC_9H_6N]$, in which the negative



Scheme 1. Preparation of the Complex.



Scheme 2. Configurational isomers of the complex.

charge can delocalize to the conjugated quinoline ring, and an intermediate MoO_2^{2+} may be formed. Finally, the combination of the two intermediates results in the formation of the complex. The proportion of reagents is important; reactions with other proportions of reagents have been carried out, but did not produce the title complex. Investigation on the detailed mechanism is underway in our lab.

Compared with methods to synthesize dioxomolybdenum complexes using reagents containing MoO_2^{2+} [20–23], our reaction presents another route employing polymolybdate clusters as Mo-releasing reagents *via* disassembly of polymolybdate anions. The reaction may also be extended to the synthesis of dioxotungsten analogs.

3.2. *X-ray crystal structural studies*

The structure of the complex was established by single-crystal X-ray analysis. It crystallizes in the monoclinic system with space group *P*21/*c*. An ORTEP drawing along with the atom labeling scheme is depicted in figure 1. A summary of the crystallographic data and structural determination is provided in table 1. Selected bond lengths and angles are listed in table 2. The molecule is mononuclear, exhibiting a distorted octahedral geometry, in which each oxo ligand is located *trans* to a quinolyl nitrogen of each amido ligand. 8-Aminoquinoline ligates to Mo(VI) in an *N,N*-chelating manner forming stable five-membered rings.

The molecule is located on the crystallographic two-fold axis bisecting the O–Mo–O angle and two crystallographically independent molecules are present in the unit cell. The Mo=O distances (1.711, 1.717 Å) are within the range typical for oxomolybdenum units [29]. Owing to the strong *trans* effect of oxo, the observed $Mo–N_{quinolyl}$ bond distances (2.338, 2.352 Å) of the complex are relatively long (>2.30 Å), comparable to the $Mo–N_{pyridyl}$ distances in analogous with pyridine-functionalized amido ligands [27]. The amido nitrogens are sp^2-hybridized with the p-orbital orthogonal to the trigonal plane, giving an approximately planar environment and Mo–N (d←p) π-bonding interactions. The $Mo–N_{amido}$ bond distances (2.023, 2.041 Å) are shorter than the calculated M–N single bond distance of 2.05 Å due to the Mo–N (d←p) π-interactions. Compared with the $Mo–N_{amido}$ bond distances of 2.076(2)–2.077(2) Å in $[MoO_2(N(SiMe_3)(2\text{-}C_5H_3N\text{-}6\text{-}Me))_2]$ and 2.074(2)–2.076(2) Å in $[MoO_2(N(SiBu\mathit{t}Me_2)(2\text{-}C_5H_3N\text{-}6\text{-}Me))_2]$ [27], the $Mo–N_{amido}$ bond distances of the complex are shorter because Mo–N (d←p) π-interactions are much weaker in the two analogs due to Si–N π-interactions.

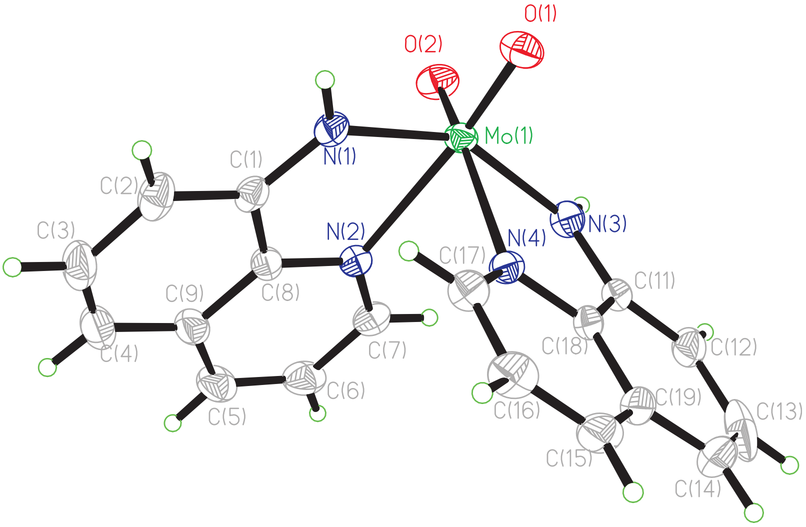


Figure 1. ORTEP drawing along with the atom labeling scheme for the complex.

Table 1. Summary of crystallographic data for the complex.

Empirical formula	$[MoO_2(HNC_9H_6N)_2]_2[DMF]_2$
Formula weight	487.37
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*P*21/*c*
Unit cell dimensions (Å, °)	
a	25.037(5)
b	10.020(2)
c	17.756(4)
α	90°
β	110.60(3)°
γ	90°
Volume, *z*	4169.4(14), 8
Calculated density ($Mg\,m^{-3}$)	1.553
Absorption coefficient (mm^{-1})	0.662
F(000)	1984
Crystal size (mm^3)	0.49 × 0.19 × 0.07
θ range for data collection	0.87–27.67°
Limiting indices	$-32 \le h \le 32$, $-12 \le k \le 13$, $-23 \le l \le 21$
Reflections collected	30,983
Independent reflection	9577 [*R*(int) = 0.0357]
Completeness to $\theta = 25.00$ (%)	99.7
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.95 and 0.86
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9577/0/541
Goodness-of-fit on F^2	1.052
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0559$, $wR_2 = 0.1410$
R indices (all data)	$R_1 = 0.0793$, $wR_2 = 0.1540$
Largest difference peak and hole ($e\,Å^{-3}$)	3.523 and −0.744

Table 2. Selected bond distances (Å) and angles (°) for the complex.

Mo(1)–O(1)	1.711(3)	N(1)–C(1)	1.362(6)
Mo(1)–O(2)	1.717(3)	N(2)–C(7)	1.330(5)
Mo(1)–N(1)	2.023(4)	N(2)–C(8)	1.350(6)
Mo(1)–N(3)	2.041(4)	N(4)–C(17)	1.324(5)
Mo(1)–N(4)	2.338(4)	N(4)–C(18)	1.368(6)
Mo(1)–N(2)	2.352(4)	N(3)–C(11)	1.364(6)
O(1)–Mo(1)–O(2)	106.73(16)	N(1)–Mo(1)–N(4)	83.51(14)
O(1)–Mo(1)–N(1)	91.43(15)	N(3)–Mo(1)–N(4)	71.99(14)
O(2)–Mo(1)–N(1)	107.07(16)	O(1)–Mo(1)–N(2)	160.93(14)
O(1)–Mo(1)–N(3)	105.84(16)	O(2)–Mo(1)–N(2)	87.42(14)
O(2)–Mo(1)–N(3)	92.29(16)	N(1)–Mo(1)–N(2)	71.86(13)
N(1)–Mo(1)–N(3)	149.29(15)	N(3)–Mo(1)–N(2)	85.82(14)
O(1)–Mo(1)–N(4)	88.61(15)	N(4)–Mo(1)–N(2)	80.60(12)
O(2)–Mo(1)–N(4)	160.77(14)	–	–

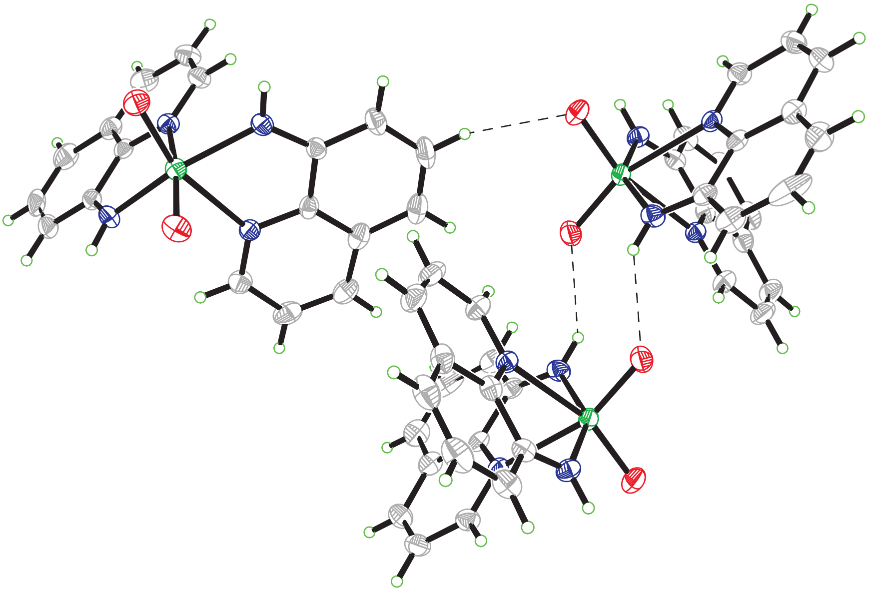


Figure 2. Basic hydrogen-bonding building block of the complex.

Intermolecular hydrogen bonding among neighboring molecules plays an important role in cell packing. One molecule and one neighbor are connected into zigzag chains *via* C–H $\cdots$ O hydrogen bonds. Those chains are further connected into networks through interchain N–H $\cdots$ O hydrogen bonds (figures 2 and 3). An eight-membered ring containing two hydrogen-bonding donors and two acceptors, defined as $R_2^2(8)$ according to hydrogen-bonding graph set, is formed.

3.3. *Spectroscopic characterization*

UV-Vis spectrum of the complex was recorded in DMF at room temperature. The electronic spectrum in DMF displays three absorption bands at 270, 344, and

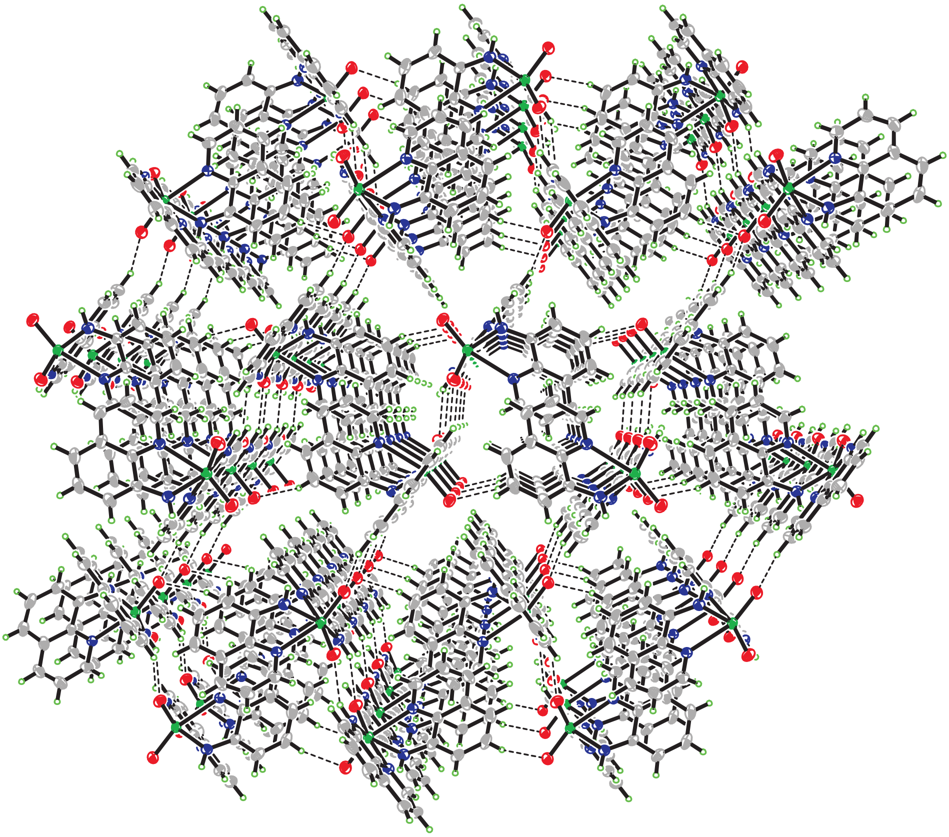


Figure 3. Hydrogen-bonding network of the complex.

445 nm, assigned as charge-transfer transitions of the type $N_{quinolyl}(p\pi)$–$Mo(p\pi)$ LMCT, $O(p\pi)$–$Mo(d\pi)$ LMCT, and $N_{amido}(p\pi)$–$Mo(d\pi)$ LMCT, respectively [30, 31]. The presence of three bands indicates the formation of Mo=O, $Mo–N_{quinolyl}$, and $Mo–N_{quinolyl}$ bonds, further confirmed by crystal structure studies.

IR spectrum of the complex shows two strong ν(Mo=O) bands at 912 and 870 cm^{-1}, characteristic of the symmetric and asymmetric stretching vibrations of the *cis*-MoO_2 fragment [31, 32]. The other bands in the IR spectrum are attributed to bound ligand. The band at 3340 cm^{-1} is assigned to N–H stretch. The band at 3040 cm^{-1} is assigned to the C–H stretch of quinoline while four bands at 1573, 1506, 1470, and 1340 cm^{-1} are diagnostic for the quinoline framework.

4. Conclusion

We report a new mononuclear *cis*-dioxo-Mo(VI) complex containing two 8-aminoquinolines. Other than the popular route to dioxomolybdenum complexes using reagents containing MoO_2^{2+}, such as $[MoO_2Cl_2]$ and $[MoO_2(acac)_2]$, we found a new reaction of $(Bu_4N)_2[Mo_6O_{19}]$ with 8-aminoquinoline in the presence of DCC afforded the dioxo-Mo(VI) complex, $[MoO_2(NH\text{-}C_9H_6N)_2]$. The reaction presents another route using polymolybdate clusters as Mo-releasing reagents to synthesize such complexes. In the structure, each oxo is located *trans* to the quinolyl nitrogen and the amido ligands are bound to the metal center in an *N,N*-chelating fashion. Furthermore, the molecules form zigzag chains and the chains are further connected into networks through hydrogen bonds.

Supplementary material

Crystallographic data for the complex have been deposited with the Cambridge Crystallographic Data Center as supplementary publications, CCDC reference number 800360. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223/336 033; Email: deposit@ccdc.cam.ac.uk).

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