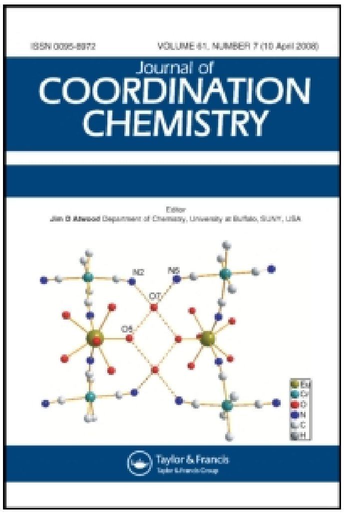

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Monodentate imido and bidentate aminophenolate coordination of 2-aminophenol in rhenium(V) complexes

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Reactions of *trans*-[$ReOCl_3(PPh_3)_2$] and *trans*-[$ReO(OEt)I_2(PPh_3)_2$] with 2-aminophenol (H_2ap) in acetonitrile led to the formation of *cis*-[$ReOCl_2(Hap)(PPh_3)$] (**1**) and *trans*-[$Re(ap)(Hap)I(PPh_3)_2$]I (**2**), respectively. The X-ray crystal structures show that Hap is coordinated as a bidentate chelate *via* the neutral amino nitrogen and deprotonated phenolate oxygen, and ap is coordinated as a monodentate through the imido nitrogen. The complexes have been characterized by IR spectroscopy, NMR spectrometry and X-ray crystallography. The bite angle of the Hap chelate is 76.9(1)° and 76.0(1)° in **1** and **2**, respectively.

Keywords: Rhenium(V); Crystal structures; Aminophenolate; Imido

1. Introduction

Current interest in the coordination chemistry of rhenium is mainly due to the possible application of compounds of the $^{186/188}Re$ isotopes as therapeutic radiopharmaceuticals [1]. We have studied for some time the reactivity of monooxo and dioxorhenium(V) cores with the aromatic diamine 1,2-diaminobenzene and its derivatives. We have shown that diaminobenzene coordinates in a variety of different forms to rhenium, as a bidentate diamide [2, 3], bidentate aminoamide [4], bidentate semibenzoquinone diimine [5] and as a monodentate imide [6]. We have since extended this project to 2-aminophenol (H_2ap) and its derivatives. For example, the potentially ambidentate 2,3-diaminophenol (H_2dap) coordinates to rhenium(V) only *via* a doubly deprotonated amino nitrogen, as an imide, in [$Re(dap)Cl_3(PPh_3)_2$] [6].

Here we report the synthesis and characterization of the complexes *cis*-[$ReOCl_2(Hap)(PPh_3)$] (**1**) and *trans*-[$Re(ap)(Hap)I(PPh_3)_2$]I (**2**). Complex **1** was prepared from *trans*-[$ReOCl_3(PPh_3)_2$] and **2** from *trans*-[$ReO(OEt)I_2(PPh_3)_2$];

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cis-diiodo complexes of rhenium(V) have never been observed, because of the steric bulk of iodide as ligand.

2. Experimental

Trans-[ReOCl$_3$(PPh$_3$)$_2$] [7] and *trans*-[ReO(OEt)I$_2$(PPh$_3$)$_2$] [8] were prepared by literature procedures. H$_2$ap was obtained commercially (Aldrich). Solvents were refluxed over appropriate drying agents, and distilled and degassed before use. IR spectra were obtained using KBr disks and ^{1}H NMR spectra were run in d$_6$-DMSO at ambient temperatures. The instrumentation used is the same as reported earlier [9].

2.1. *Cis-[ReOCl$_2$(Hap)(PPh$_3$)] · CH$_3$CN (1 · CH$_3$CN)*

Trans-[ReOCl$_3$(PPh$_3$)$_2$] (113 mg, 135 µmol) and H$_2$ap (31 mg, 284 µmol) were dissolved in 20 cm^3 of acetonitrile. The mixture was heated at reflux for 90 min, during which time the colour of the solution turned green. After cooling to room temperature, the solution was filtered and left to evaporate slowly. After 3 days, green crystals suitable for X-ray crystallography were recovered, washed with cold acetonitrile ($3 \times 2\,\mathrm{cm}^2$) and diethylether, and dried under vacuum. Yield: 57 mg (73%); m.p. 227°C. Anal. Calcd for C$_{26}$H$_{24}$N$_2$O$_2$Cl$_2$PRe (%): C, 45.62; H, 3.53; N, 4.09. Found: C, 46.06; H, 3.55; N, 4.16. IR (cm^{-1}): ν(N–H) 3204, 3241; ν(Re=O) 973; ν(C–O) 1268; ν(Re–N) 532; ν(Re–O) 444; ν(Re–Cl) 332, 345. ^{1}H NMR (δ, ppm): 10.81 (1H, br s, NH), 9.99 (1H, br s, NH), 7.71–7.38 (15H, m, PPh$_3$), 7.37 (1H, d, H(6)), 7.23 (1H, t, H(4)), 7.07 (1H, d, H(3)), 6.87 (1H, t, H(5)).

2.2. *Trans-[Re(ap)(Hap)I(PPh$_3$)$_2$]I (2)*

The complex was prepared by the same method as for **1** by using *trans*-[ReO(OEt)I$_2$(PPh$_3$)$_2$] and a twofold molar excess of H$_2$ap. Yield: 62%; m.p. 273°C. Anal. Calcd for C$_{48}$H$_{41}$N$_2$O$_2$I$_2$P$_2$Re (%): C, 48.87; H, 3.50; N, 2.37. Found: C, 49.01; H, 3.49, N, 2.69. IR (cm^{-1}): ν(N–H) 3118, 3155, 3190; ν(O–H) 3329; ν(Re=N) 1095; ν(C–O) 1245; ν(Re–N) 527; ν(Re–O) 434; ν(Re–I) 275. ^{1}H NMR (δ, ppm): 10.96 (1H, br s, NH), 8.75 (1H, br s, NH), 8.18–7.47 (35H, m), 7.43 (1H, d), 6.95 (1H, d), 6.46 (1H, t).

2.3. *Crystallography*

Data collection was performed on a Nonius Kappa CCD diffractometer at 200 K with Mo-Kα radiation ($\lambda = 0.71073\,\text{Å}$). The structures were solved by direct methods applying SIR97 [10] and refined by least-squares procedures using SHELXL97 [11]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated in idealized geometrical positions. Data were corrected by a numerical absorption correction [12] after optimizing the crystal shape with XShape [13]. There are two molecules of **2** in the asymmetric unit. Crystal and structure refinement data are given in table 1. Selected bond lengths and angles are given in table 2.

Table 1. Crystal data and structure refinement data for **1** and **2**.

	1	**2**
Chemical formula	$C_{26}H_{24}N_2O_2Cl_2PRe$	$C_{48}H_{41}N_2O_2I_2P_2Re$
Formula weight	684.57	1179.81
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions (Å, °)	$a = 9.9003(5)$	11.1463(1)
	$b = 9.9734(5)$	20.8233(2)
	$c = 26.169(2)$	21.9010(2)
	α	62.2284(4)
	$\beta = 92.527(7)$	80.4354(4)
	γ	88.9227(4)
Volume (Å^3)	2581.4(2)	4425.2(1)
Z	4	4
Density (Calcd) (Mg m^{-3})	1.761	1.771
Absorption coefficient (mm^{-1})	5.003	4.254
$F(000)$	1336	2280
Crystal size (mm^3)	$0.07 \times 0.12 \times 0.26$	$0.04 \times 0.07 \times 0.15$
θ range for data collection (°)	2.2–28.0	3.2–27.5
Index ranges	$-12 \le h \le 12$	$-14 \le h \le 14$
	$-13 \le k \le 13$	$-27 \le k \le 27$
	$-34 \le l \le 34$	$-26 \le l \le 28$
Reflections measured	21945	71481
Independent/observed reflections	6179/4835	20078/16763
Data/parameters	6179/392	20078/1027
Goodness-of-fit on F^2	0.93	1.03
Final R indices [$I > 2.0\sigma(I)$]	0.0280($wR_2 = 0.0614$)	0.0360 ($wR_2 = 0.0911$)
Largest diff. peak/hole (e Å^{-3})	0.97/−1.44	1.47/−2.18

3. Results and discussion

3.1. *Synthesis*

The reaction of *trans*-$[ReOCl_3(PPh_3)_2]$ with a twofold molar excess of 2-aminophenol (H_2ap) in boiling acetonitrile resulted in the complex $[ReOCl_2(Hap)(PPh_3)]$ (**1**), according to the following equation:

$$\left[ReOCl_3(PPh_3)_2\right] + H_2ap \rightarrow \mathbf{1} + PPh_3 + HCl$$

Experimental evidence suggests that Hap is present in **1** as a bidentate monoanionic chelate with coordination through the neutral amino nitrogen and deprotonated phenolic oxygen. Complex **1** is a non-electrolyte in DMF, and it is weakly soluble in chloroform, DMF and DMSO. However, by changing the starting material to *trans*-$[ReO(OEt)I_2(PPh_3)_2]$, the rhenium(V) complex salt $[Re(ap)(Hap)I(PPh_3)_2]I$ (**2**) was isolated. The Hap ligand is again coordinated in a bidentate fashion *via* the neutral amino nitrogen and deprotonated phenolic oxygen, but ap coordinates as a monodentate *via* the doubly deprotonated amino nitrogen, which is therefore present as an imide,

$$\left[ReO(OEt)I_2(PPh_3)_2\right] + 2H_2ap \rightarrow \mathbf{2} + EtOH + H_2O$$

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

		1	
Re–O(1)	1.973(3)	Re–O(2)	1.683(3)
Re–N(1)	2.190(4)	Re–P	2.449(1)
Re–Cl(1)	2.424(1)	Re–Cl(2)	2.344(1)
O(1)–C(1)	1.354(5)	N(1)–C(2)	1.457(5)
O(1)–Re–O(2)	162.4(1)	N(1)–Re–Cl(2)	167.77(9)
O(2)–Re–Cl(1)	99.2(1)	O(2)–Re–Cl(2)	104.7(1)
O(1)–Re–P	90.48(9)	O(2)–Re–N(1)	87.0(1)
Re–O(1)–C(1)	120.6(2)	Re–N(1)–C(2)	110.2(2)
O(1)–Re–N(1)	76.9(1)	Cl(1)–Re–Cl(2)	90.18(4)

	2	
	Molecule A	Molecule B
Re–O(1)	1.996(3)	2.024(3)
Re–N(2)	1.729(4)	1.717(3)
Re–N(1)	2.233(3)	2.204(4)
Re–P(1)	2.483(1)	2.491(1)
Re–P(2)	2.494(1)	2.501(1)
Re–I(1)	2.7197(4)	2.7250(4)
C(1)–O(1)	1.359(6)	1.368(6)
C(7)–N(2)	1.373(5)	1.378(6)
C(2)–N(1)	1.463(5)	1.452(6)
O(1)–Re–N(2)	168.7(2)	168.9(2)
N(2)–Re–N(1)	92.8(2)	92.6(2)
N(2)–Re–P(1)	93.2(1)	91.6(1)
N(2)–Re–P(2)	93.7(2)	92.5(1)
N(2)–Re–I(1)	101.6(1)	101.4(1)
Re–N(2)–C(7)	170.8(3)	170.2(4)
Re–N(1)–C(2)	110.7(3)	111.6(3)
P(1)–Re–P(2)	173.09(4)	175.94(4)

The formation of **2** is somewhat unexpected, since rhenium(V) has a propensity to form neutral complexes. However, a neutral complex would necessarily imply two iodides coordinated *cis* to each other, which would be difficult to achieve if the steric bulk of iodide is taken into account. Compound **2** is air stable and a 1 : 1 electrolyte in DMF. It dissolves in the polar solvents DMSO and THF to give green solutions that are stable for days.

3.2. *Spectroscopic characterization*

The IR spectrum of **1** displays the Re=O stretching frequency as a sharp band at 973 cm^{-1}, at the higher end of the range normally found for this kind of bond [14]. Two medium intensity bands at 3204 and 3241 cm^{-1} are indicative of the presence of a coordinated neutral NH$_2$ group. The ν(Re–O) stretch appears at 444 cm^{-1}, which intimates that the anionic phenolate oxygen is coordinated *trans* to the oxo group. The two ν(Re–Cl) values at 332 and 345 cm^{-1} indicate *cis* chlorides coordinated in the equatorial plane and *cis* to the oxo oxygen. Three medium intensity bands at 3118, 3155 and 3190 cm^{-1} are observed for ν(N–H) in the IR spectrum of **2**, and the presence of the uncoordinated hydroxyl group of ap is indicated by a broad band at 3329 cm^{-1}. A strong sharp band at 1095 cm^{-1} is assigned to ν(Re=N).

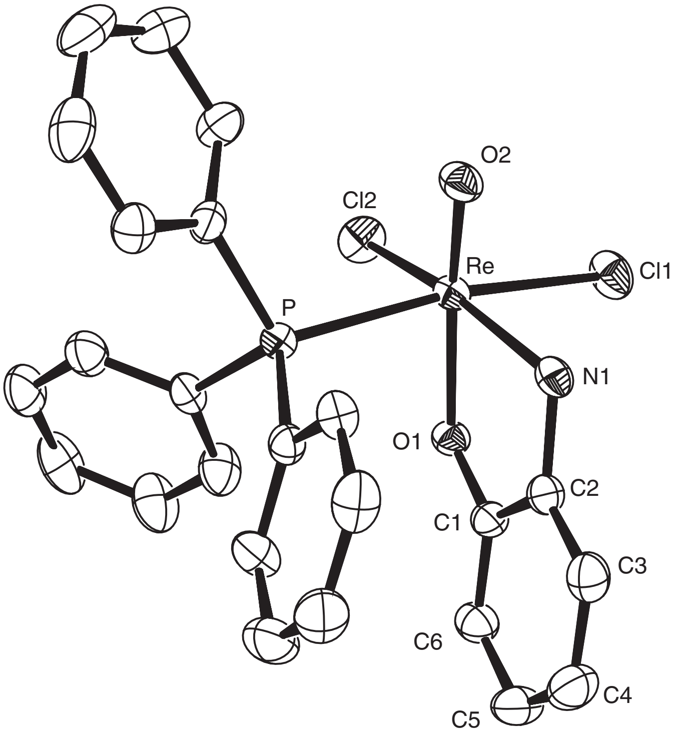

Figure 1. An ORTEP view of [$ReOCl_2(Hap)(PPh_3)$] (**1**) showing the atom labelling (40% probability ellipsoids).

The two amino hydrogens in **1** and **2** appear as two broad singlets downfield around δ 11 and 8–9 ppm in ^1H NMR spectra. The four aromatic protons of Hap in **1** appear as well-resolved doublet-triplet-doublet-triplet signals in the range δ 7.37–6.87 ppm. All aromatic proton signals (except three) of the Hap and ap ligands in **2** are obscured by the peaks of the phosphine protons, and a full assignment could not be made, although the spectrum integrates for 41 protons.

3.3. *Structure of cis-[$ReOCl_2(Hap)(PPh_3)$] (1)*

The structure of **1** (figure 1) exhibits distorted octahedral geometry around rhenium(V). The basal plane is defined by the amino nitrogen of the Hap ligand, two chlorides and the phosphorus atom of PPh_3, with the phenolate and oxo oxygens in *trans* axial positions. The two chlorides are coordinated *cis* to each other, with the Cl–Re–Cl angle practically orthogonal at 90.18(4)°. Distortion from an ideal octahedron mainly results in a non-linear O(2)=Re–O(1) axis of 162.4(1)°, accomplished by P–Re–Cl(1) and N(1)–Re–Cl(2) angles of 170.34(3)° and 167.8(1)°, respectively. The rhenium atom is shifted out of the mean equatorial Cl_2PN plane by 0.214 Å towards the oxo oxygen O(2), which is the result of the non-orthogonal angles O(2)–Re–Cl(1) = 99.2(1)°, O(2)–Re–Cl(2) = 104.7(1)°, O(2)–Re–P = 90.48(9)° and O(2)–Re–N(1) = 87.0(1)°. In the O_2Cl_2NP polyhedron the rhenium atom is 1.00 Å from the Cl(1)O(2)Cl(2) plane and 1.36 Å from PO(1)N(1), the dihedral angle being 9.40°.

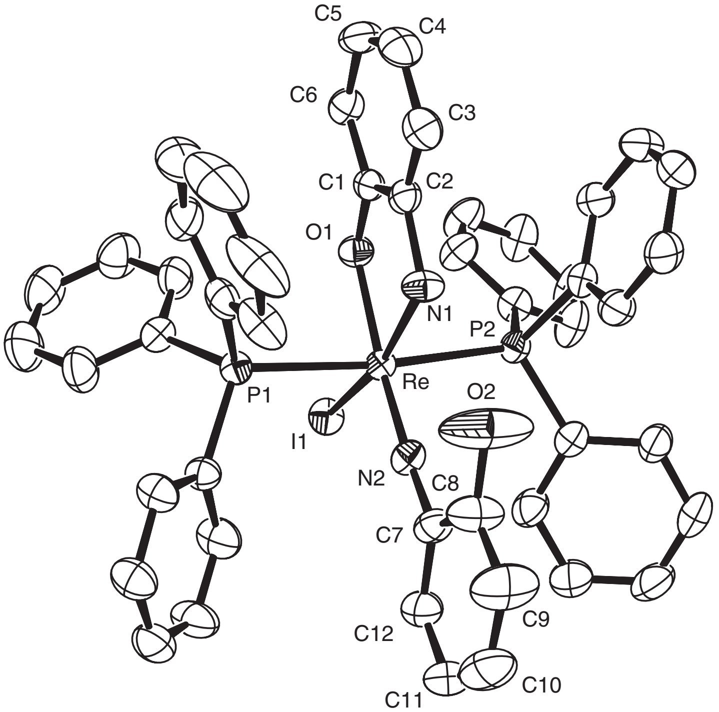

Figure 2. A view of $[Re(ap)(Hap)I(PPh_3)_2]^+$ showing the atom numbering scheme (40% probability ellipsoids).

The Re–Cl(1) bond *trans* to P, at 2.424(1) Å, is significantly longer than the chloride *trans* to amine N(1) [2.344(1) Å], which confirms the higher *trans* influence of the phosphine group. The Re–O(1) distance of 1.973(3) Å is very similar to other Re(V)–O (phenolate) distances [14, 15], demonstrating that the oxygen atom acts as a monoanionic donor. Other bond distances and angles are normal (table 2).

3.4. *Structure of trans-[Re(ap)(Hap)I(PPh₃)₂]I (2)*

X-ray crystallographic analysis of **2** shows that two molecules of the complex (**A** and **B**) exist in the asymmetric unit. These have different orientations in the lattice, and their equatorial coordination planes P_2NI make a dihedral angle of 63.84° with each other. They have comparable bond distances and angles (table 2). The molecular structure is illustrated in figure 2. The rhenium atom lies at the centre of a distorted octahedron. The basal plane is defined by the neutral amino group of Hap, two phosphorus atoms and the iodide. The Re atom lies 0.23 Å out of this mean plane towards N(2). The monoanionic phenolate oxygen and the doubly deprotonated imido nitrogen N(2) of ap are in *trans* axial positions. Two triphenylphosphine ligands are coordinated to the metal centre *trans* to each other, with the P(1)–Re–P(2) angle close to linearity [173.09(4)° in **A**, 175.94(4)° in **B**]. The average Re–P distance equals 2.492(1) Å, which is significantly longer than in **1**, but similar to other rhenium(V) complexes with a *trans* biphosphine arrangement [average 0.489(3) Å] [6, 16]. Iodide is rarely

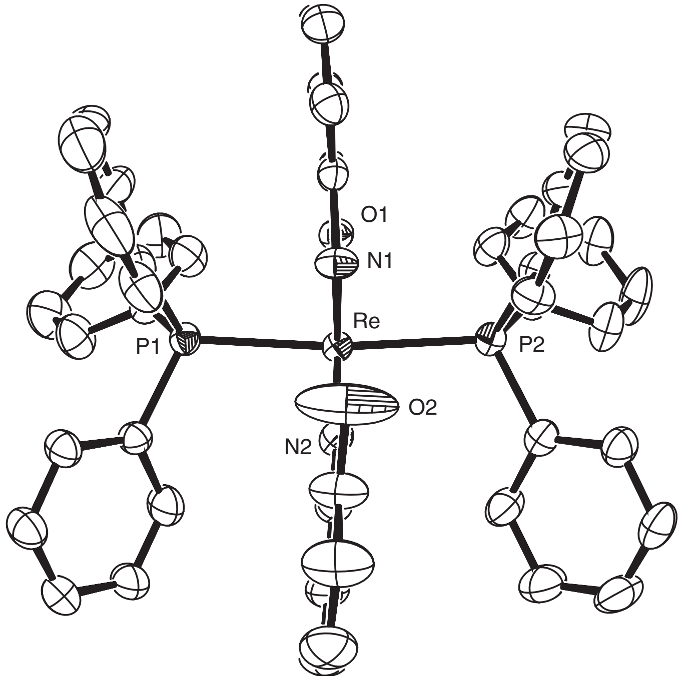

Figure 3. Position of the C(1)–C(6) ring of **2** relative to the phenyl rings of PPh_3 (40% probability ellipsoids).

found as a ligand in rhenium(V) complexes, and the Re–I average distance in **A** and **B** of 2.7224(4) Å falls in the observed range of 2.664(2)–2.789(3) Å [8]. The iodide is coordinated *trans* to the neutral N(1) of Hap, with which it makes an average angle of 165.7(1)°.

The ap ligand acts as a monodentate dianion, with coordination to rhenium through the doubly deprotonated imido nitrogen N(2) only and the O(2)H hydroxyl group is not coordinated. The Re–N(2)–C(7) average bond angle of 170.5(4)° illustrates a significant deviation from linearity of the coordination mode of the triply bonded phenylimido unit, and the average Re–N(2) distance of 1.723(4) Å agrees with values found in other rhenium(V)-phenylimido octahedral complexes [17, 18]. The phenylimido moiety is virtually perpendicular to the mean equatorial plane (dihedral angle 174.7°). In addition, there are three effective intramolecular hydrogen bonds that consolidate the crystal packing. In particular, the N(1)–H(1B) ⋯ O(2) and O(2)–H ⋯ N(1) separations are both equal to 2.799(5) Å. Similarly, the O(2)–H(2) ⋯ N(2) distance is 2.656(6) Å and the O(2)–H(2) ⋯ N(2) angle is 119.1°.

Hap acts as a monoanionic bidentate, with coordination through the neutral amino group $N(1)H_2$ (*trans* to the iodide) and the deprotonated phenolate oxygen O(1). The O(1)–Re–N(2) bond deviates considerably from linearity [168.8(2)° average in **A** and **B**], and the average O(1)–Re bond distance of 2.010(3) Å is close to the average for phenolate oxygen bonds *trans* to phenylimido groups [2.026(8) Å] [15]. The average Re–N(1) bond of 2.219(4) Å is close to that found for $Re–NH_2$ bonds [15], and the average Re–N(1)–C(2) bond angle of 111.2(3)° is close to what is expected for the sp^3 hybridized nitrogen of the amino group. C–N bond distances of ap and

Hap differ considerably. The average C(2)–N(1) distance of Hmap equals 1.458(6) Å, as expected for a single bond. However, the C(7)–N(2) distance of 1.376(6) Å indicates considerable double bond character.

To minimize steric congestion around the rhenium atom, the Hap ligand fits between two phenyl rings (figure 3), so that the C(1)–C(6) ring centroid is 3.78 Å from the C(19)–C(24) centroid and 3.48 Å from that of C(37)–C(42), and it makes dihedral angles of 16.1° and 16.4° with the first and second phenyl rings, respectively. The monodentate coordination of ap in complex **2** is unusual and surprising. A similar coordination mode was however found for 3-methyl-2-aminophenol [19]. Imido coordination by 3-methyl-1,2-diaminobenzene was also observed in the reaction of the diamine and *trans*-[$ReOCl_3(PPh_3)_2$] in ethanol [6].

Supplementary material

CCDC-280613 (for **1**) and CCDC-280614 (for **2**) contain crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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