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## Hydrothermal synthesis and solid-state structure of $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$

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Dedicated to the memory of Michelle Millar, an outstanding synthetic chemist, chemistry pioneer, and a good friend. Her smile, sense of humor, generosity, and enthusiasm for inorganic chemistry are sorely missed.

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### ABSTRACT

$\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$  is a key starting material for further explorations of dinuclear technetium(III) chemistry and is obtained in 70% yield from readily available starting materials via hydrothermal techniques. Its single crystal X-ray structure reveals the familiar paddle-wheel motif of four bridging acetate groups spanning a short Tc–Tc bond (2.1758(3) Å), augmented by axial chlorides at a Tc–Cl separation of 2.5078(4) Å. The Tc–Tc quadruple bond length is slightly shorter than the one found in the pivalate derivative,  $\text{Tc}_2(\text{O}_2\text{CCMe}_3)_4\text{Cl}_2$  (2.192(1) Å), and slightly longer than found in  $[\text{Tc}_2(\text{O}_2\text{CCH}_3)_4](\text{TcO}_4)_2$  (2.149(1) Å), the only other structurally characterized members of the small family of  $\text{Tc}_2(\text{O}_2\text{CR})_4\text{X}_2$  dimers.

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### 1. Introduction

Technetium occupies a central position among the transition elements. Because it bears a close electronic relationship to its heavier congener rhenium, the occurrence of analogous compounds is expected, but the radioactive nature of technetium has served to limit the development of its chemistry relative to that of rhenium [1]. Today, the number of laboratories worldwide that are equipped to pursue synthetic chemistry with the most readily available isotope, viz., <sup>99</sup>Tc, is severely limited. For the past several years, we have been exploring the fundamental chemistry of technetium, including that associated with metal–metal bonded dimers with bonds of order 4, 3.5 and 3 [2]. We have found many similarities between the dinuclear chemistry of Tc and Re, but also subtle and sometimes frustrating differences in the synthetic chemistry that are likely a manifestation of the redox properties of the respective elements in equivalent oxidation states. One compound that we have found to be a very useful starting material for

investigations of both dinuclear technetium(III) chemistry and as a precursor to  $\mu\text{-TcCl}_3$  ( $\text{Tc}_3\text{Cl}_9$ ) is the acetate bridged dimer,  $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$  (**1**) [3]. Its rhenium analog,  $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$ , first prepared by Taha and Wilkinson [4], played a key role at the beginning of the multiple metal–metal bond field and was an early example of a  $d^4\text{-}d^4$  dimer with a quadruple metal–metal bond.

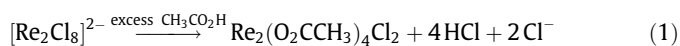
In this paper, we describe a reliable, high-yield synthesis of **1** and its characterization by single crystal X-ray diffraction. Complex **1** was first reported in the Russian literature in 1980 [5]. Subsequently, some details on its preparation using hydrothermal techniques were provided in a 1981 Russian patent [6]. A handful of additional publications dealing with **1** and its bromide analog have appeared since the patent and alternative methods for its preparation have been described. Preetz et al. [7] modeled their synthesis of **1** after that used by Cotton et al. to prepare  $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$  (Eq. (1)) [8]. This reaction provides **1** in about 40% yield, but requires the prior preparation of  $[n\text{-Bu}_4\text{N}]_2[\text{Tc}_2\text{Cl}_8]$  (**2**). Complex **2** is accessible in comparable yield (40–50%) from ammonium pertechnetate, but the synthesis involves four steps and takes a minimum of 2 days. Given the fact that both reactions are performed on a small scale, an overall yield of **1** on the order of 20% is far from satisfactory. Two other technetium(III) tetracarboxylate complexes are known, but both were isolated in low yield. The tetrapivalate,  $\text{Tc}_2(\mu\text{-O}_2\text{CCMe}_3)_4\text{Cl}_2$ , was prepared from the reaction of  $(\text{NH}_4)_3\text{Tc}_2\text{Cl}_8$  with molten pivalic acid [9], and the novel pertechnetate-capped tetraacetate,  $[\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4](\text{TcO}_4)_2$ , was

*Abbreviations:* SC-XRD, single crystal X-ray diffraction; EXAFS, extended X-ray absorption fine structure; FTIR, Fourier transform infrared spectroscopy; DWF, Debye–Waller factor.

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isolated from the aerial oxidation of solutions containing the mixed-valent dimer  $[\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2]^{1-}$  [10].



## 2. Experimental

### 2.1. Starting materials

**Caution.** Technetium-99 is a weak beta emitter ( $E_{\text{max}} = 292$  keV). All manipulations were performed in a laboratory designed for chemical synthesis with radionuclides using efficient HEPA-filtered fume hoods, Schlenk and glove box techniques, and following locally approved radioisotope handling and monitoring procedures. Ammonium pertechnetate,  $\text{NH}_4[{}^{99}\text{TcO}_4]$ , was purchased from Oak Ridge National Laboratory. It was purified and converted to  $\text{KTCO}_4$  by reaction with aqueous KOH and 30%  $\text{H}_2\text{O}_2$  as described by Busey et al. [11].

Other reagents were purchased from Sigma Aldrich and Fisher Scientific and used without further purification. High purity hydrogen gas was purchased from Praxair and used as received.

### 2.2. Synthesis of $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$ (**1**)

The synthesis of  $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$  was a local modification of the procedure reported by Rezvov et al. [6]. To a 20 mL glass scintillation vial was added  $\text{KTCO}_4$  (55.0 mg, 0.27 mmol) and an 18 mL mixture of glacial acetic acid and concentrated hydrochloric acid (2:1 by volume). The vial was loosely capped with an inverted 10 mL Teflon cup and placed inside of a 100 mL fused quartz beaker with cover. This dual containment, depicted in Fig. 1, allows for gases to permeate the reaction mixture and minimizes the spread of technetium to the autoclave. The apparatus is sealed in a 300 mL Parr Instruments 5521 series high pressure autoclave. The autoclave was purged two times with 5 atm of  $\text{H}_2$ , filled to a starting pressure of 35 atm  $\text{H}_2$ , and then heated to 210 °C at 5 °/min. After 14 h, the heater was switched off and the autoclave was allowed to cool slowly to room temperature. At that point, the autoclave was carefully depressurized and opened to reveal a deep red-orange

mother liquor covering a crop of dark red elongated hexagonal crystals. The air-stable product was rinsed with acetic acid, followed by isopropyl alcohol, and diethyl-ether, and allowed to dry in air. The reaction produced 48.1 mg (0.095 mmol) of **1** for a yield of 70%, a significant improvement over the 51% yield reported in the patent [6]. The compound is insoluble in common organic solvents (e.g., acetone, acetonitrile, tetrahydrofuran, and methylene chloride) and aqueous acids including hydrochloric, sulfuric, and acetic, but dissolves under alkaline conditions consistent with the observations of Zaitseva et al. [5]. An FTIR spectrum of **1** reveals COO stretches at 1441  $\text{cm}^{-1}$  (vs) and 1375  $\text{cm}^{-1}$  (vs), characteristic of bridging acetate groups and similar in energy to the analogous vibrations in  $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$ , viz., at 1456 and 1385  $\text{cm}^{-1}$ , as reported by Taha and Wilkinson [4].

### 2.3. X-ray crystallography

A dark red hexagonal crystal of  $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$  was mounted under Paratone on a Kapton cryoloop for data collection. Single crystal X-ray diffraction data were collected on a Bruker Apex II CCD diffractometer using Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The crystal was maintained at 100 K during data collection using an Oxford nitrogen cryostream system. The Apex II suite was used to perform data processing and an absorption correction performed with SADABS. Solution to the structure was performed by Direct Methods and refinement was carried out using SHELX-97 [12]. Anisotropic approximations of all atoms except hydrogen were refined against  $F^2$ , whereas the hydrogen atoms' positions were determined geometrically and refined using the riding model.

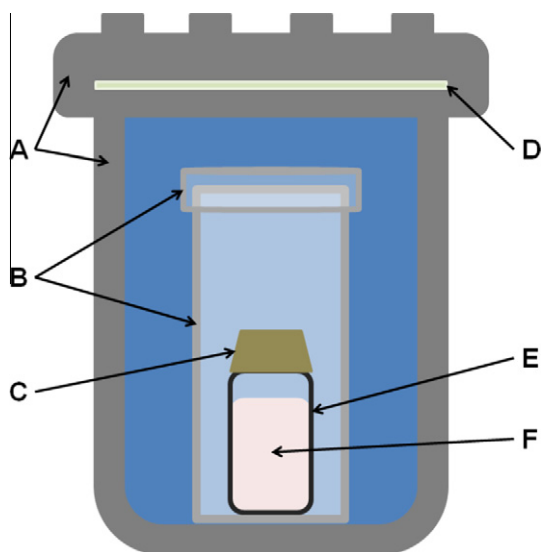
## 3. Results and discussion

### 3.1. Synthesis

Published strategies for the synthesis of binuclear (and polynuclear) technetium compounds containing multiple metal–metal

**Table 1**  
Crystallographic data and refinement parameters for  $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$  (**1**).

Crystallographic data	
Formula	$\text{C}_8\text{H}_{12}\text{Cl}_2\text{O}_8\text{Tc}_2$
Formula weight	504.90
T (K)	100
$\lambda$ (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
<i>Unit cell dimensions</i>	
a (Å)	6.4258(8)
b (Å)	8.8474(11)
c (Å)	12.5285(16)
$\alpha$ (°)	90.00
$\beta$ (°)	90.778(2)
$\gamma$ (°)	90.00
V (Å <sup>3</sup> )	712.20(15)
Z	2
Density calculated ( $\text{Mg m}^{-3}$ )	2.346
Absorption coefficient ( $\text{mm}^{-1}$ )	2.346
F(000)	488
Range of 2 $\theta$ (°)	2.82 – 30.51
Index ranges (h, k, l)	$-9 \leq h \leq 9, -12 \leq k \leq 12, -17 \leq l \leq 17$
Reflections collected	11 170
Independent reflections	2169 ( $R_{\text{int}} = 0.0277$ )
Complete to 2 $\theta$ (%)	100.0
Refinement method	full-matrix least-squares on $F^2$
Data/restraints/parameters	2169/0/93
Goodness-of-fit on $F^2$	1.076
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0180, wR_2 = 0.0467$
R indices (all data)	$R_1 = 0.0204, wR_2 = 0.0476$



**Fig. 1.** A sketch of the internal setup of the autoclave: (A) Parr Instruments 5521 series 300 mL high pressure autoclave, (B) 100 mL fused quartz beaker with cover, (C) 10 mL Teflon inverted cup used as a loose cover, (D) replaceable Teflon gasket (one use only), (E) 20 mL glass scintillation vial, (F) solution containing reactants.

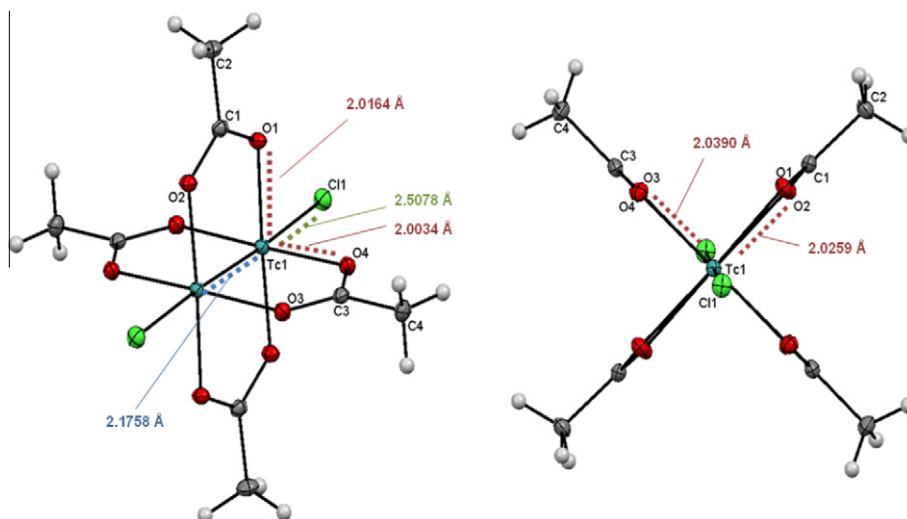


Fig. 2. X-ray crystal structure of  $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$  (**1**). The ORTEP representations display ellipsoids at the 50% probability level with key bond lengths shown.

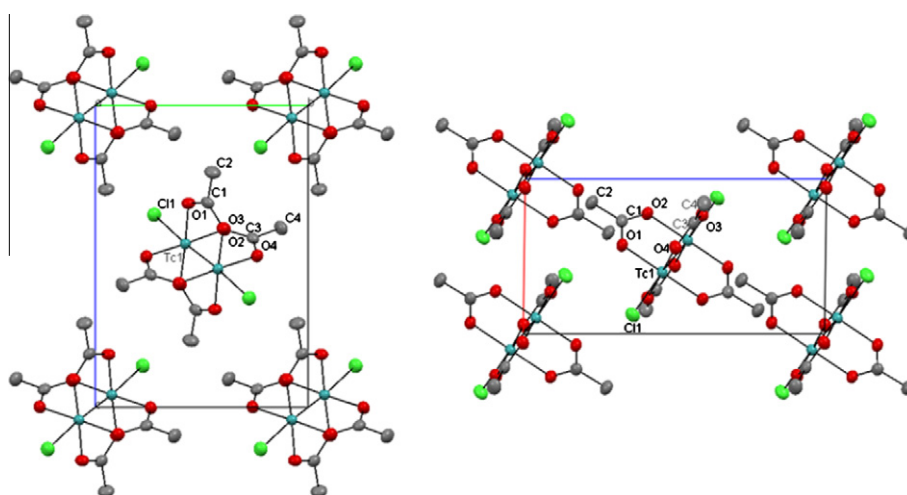


Fig. 3. Unit cell views of **1** along the *a*-axis (left image) and *b*-axis (right image). Hydrogen atoms are omitted for clarity.

bonds typically fall into one of three categories: (1) moderate temperature (100–300 °C) reduction of higher-valent mononuclear technetium precursors in aqueous hydrohalic acid solutions using molecular hydrogen (30–50 atm) as the reductant; (2) reduction of higher-valent mononuclear precursors using chemical reductants other than  $\text{H}_2$ , either in aqueous acid or non-aqueous solvents; (3) substitution and/or redox reactions involving pre-formed dinuclear complexes. Resvov and coworkers have been advocates for the first approach, while the rest of the community has traditionally opted for the latter two strategies [13]. The hydrogen reductions require the use of high-pressure stainless steel autoclaves. The use of glass test tubes and vessels inside the autoclave (vide supra) minimizes corrosion of the stainless steel. Alternatively, more corrosion resistant alloys, such as Hastelloy, can be used in place of stainless steel [14]. Kryuchkov, and others have isolated a wide variety of dinuclear and polynuclear technetium compounds by systematically varying the experimental parameters (e.g., time, pertechnetate and acid concentrations, nature of the cation, temperature, hydrogen pressure, cool-down rate, etc.), but it is fair to say that serendipity (thermodynamic self-assembly in some quarters) plays a role in the outcome of these procedures as it does in many exploratory hydrothermal syntheses [15].

Table 2

Selected bond lengths and angles for  $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$  (**1**).

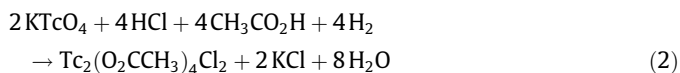
	Bond length (Å)		Bond angle (°)
Tc(1)–O(1)	2.0164(12)	O(1)–Tc(1)–O(3)	89.59(5)
Tc(1)–O(2)	2.0259(12)	O(1)–Tc(1)–O(2a)	177.47(5)
Tc(1)–O(3)	2.0390(12)	O(1)–Tc(1)–O(4a)	89.63(5)
Tc(1)–O(4)	2.0034(12)	O(1)–Tc(1)–Tc(1a)	91.22(4)
Tc(1)–Tc(1a)	2.1758(3)	Tc(1a)–Tc(1)–Cl(1)	171.903(13)
Tc(1)–Cl(1)	2.5078(4)	O(1)–Tc(1)–Cl(1)	91.12(4)
O – C (avg.)	1.280(2)	C(3)–O(3)–Tc(1)	120.94(11)
C – C (avg.)	1.484(2)	O(2)–C(1)–C(2)	120.23(15)

As mentioned above, our interest in exploring hydrothermal methods was spurred by the need for a higher yield route to **1**. We became aware of a report in the Russian patent literature that suggested that **1** was accessible from potassium pertechnetate,  $\text{KTcO}_4$ , in what could be described euphemistically as a “one-pot reaction.” Treatment of a solution of  $\text{KTcO}_4$  in a 2:1 mixture of acetic acid and concentrated aqueous hydrochloric acid with excess hydrogen for 14 h at 210 °C provides **1** in 70% yield in the form of beautiful dark red crystals that can be recovered by filtration of the mother liquor (Eq. (2)). The details of how **1** is generated

**Table 3**  
Selected interatomic distances (Å) and angles (°) for  $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$  (**1**),  $\text{Tc}_2(\mu\text{-O}_2\text{CC}(\text{CH}_3)_3)_4\text{Cl}_2$ , and  $\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$ .

Compound	<i>d</i> M–M	<i>d</i> M–Cl	<i>d</i> M–O (av.)	M–M–Cl	M–M–O (av.)	Method [Ref. #]
$\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$	2.1758(3)	2.5078(4)	2.0211(12)	171.903(13)	90.63(4)	SC-XRD, this work
	2.18(1)	2.43(1)	2.03(1)	–	–	EXAFS [17]
	2.192	2.41	2.03	–	–	Raman [18]
$\text{Tc}_2(\mu\text{-O}_2\text{CC}(\text{CH}_3)_3)_4\text{Cl}_2$	2.192(2)	2.408(4)	2.032(4)	180.00	90.67(11)	SC-XRD [9]
$\text{Re}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$	2.224(4)	2.5213(4)	2.0181(14)	176.519(5)	90.074(5)	SC-XRD [16]

during the course of this procedure are not known or obvious, but it would appear from other papers in the technetium literature that reduction of the metal below the +4 oxidation state invariably leads to coupling of metal centers and the formation of dinuclear or polynuclear clusters [13]. This process is likely encouraged by the presence of bridging acetate ligands. Once formed, **1** is insoluble in common organic solvents and the mother liquor from whence it was isolated.



### 3.2. Single crystal X-ray diffraction

Complex **1** crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 6.4258(8)$  Å,  $b = 8.8474(11)$  Å,  $c = 12.5285(16)$  Å, and  $\beta = 90.778(2)^\circ$ , broadly consistent with the isostructural Re analog [16]. Crystallographic data and refinement parameters are summarized in Table 1. The molecular structure of the compound is shown in Figs. 2 and 3. In Fig. 2, a normal view of the molecular structure shows the expected ditechneium paddle-wheel motif, capped with axial chlorines. Fig. 3 shows a unit cell along the *a*- and *b*-axes. Selected bond lengths are summarized in Tables 2 and 3. The refined Tc–Tc quadruple bond length (2.1758(3) Å) is essentially identical to the published extended X-ray absorption fine structure (EXAFS) value (Tc–Tc = 2.18(2) Å), [17] and is slightly shorter than that estimated (2.19 Å) from an analysis of the Raman spectrum [18]. It is also marginally shorter than the Tc–Tc separation reported (2.192(2) Å) for the related pivalate derivative [9].

The paddle-wheel unit is quite regular with the exception of the capping chlorides, which are bent roughly  $8^\circ$  from linear (Tc(1a)–Tc(1)–Cl(1) = 171.903(13)°). A smaller distortion ( $\sim 3.5^\circ$ ) is observed in the corresponding dirhenium analog [16], and no distortion is observed for the pivalate complex [9], which crystallizes in a tetragonal space group. We suspect that crystal packing is responsible for these small distortions. The packing for **1** is illustrated in Fig. 3. The distorted Tc–Tc–Cl angle may impact Tc–Cl distance. We find the latter to be 2.5078(4) Å, considerably longer than the estimates of 2.43(1) Å from EXAFS [17] and 2.41 Å from the Raman data [18]. In the EXAFS analysis, the number of Cl atoms attached to Tc was fixed at one, and the Tc–Cl distance and the Debye–Waller factor (DWF) for the Tc–Cl scattering were refined [17]. The DWF fit, i.e.,  $0.012 \text{ \AA}^2$ , is significantly higher than the ones reported in other Tc chloride complexes, which are typically on the order of  $0.003 \text{ \AA}^2$ . The value of the residual (difference between the experimental spectra and the fit) is also high (17%) and suggests that the fit may not be optimal. Further analysis of the EXAFS spectra of **1** by fixing the DWF to those determined in reference samples such as  $(n\text{-Bu}_4\text{N})_2\text{Tc}_2\text{Cl}_8$  and refining the distance and the number of Cl atoms will be necessary to ascertain if the Tc–Cl distance found by EXAFS spectroscopy

converges on the SC-XRD value. Table 3 summarizes important bond distances/angles determined by the various methods.

### 4. Conclusion

A reliable, high-yield method for the synthesis of  $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$  (**1**) has been developed based on a modification of an earlier report in the Russian patent literature. It is attractive because of its simplicity. Complex **1** is an important starting material for a range of other molecular and solid-state compounds of technetium(III) [3]. The X-ray structure of **1** is reported for the first time and brings to 8 the total number of structurally characterized, quadruply bonded technetium(III) dimers [2,13]. By comparison, the number of structurally characterized rhenium(III) dimers with Re–Re quadruple bonds exceeds 100 [19].

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### Appendix A. Supplementary data

Single crystal X-ray diffraction data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 890709. These data can be obtained free of charge via <http://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; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). FTIR spectrum of  $\text{Tc}_2(\mu\text{-O}_2\text{CCH}_3)_4\text{Cl}_2$  and a list of associated frequencies. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2012.09.064>.

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