

Supplementary Information

Hydrolysis of 2-phenylazophenyltellurium trihalides: isolation of an unprecedented homometallic, discrete heptanuclear organotellurium oxide cluster

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Experimental

General experimental Procedures:

Precursors **3a** and **3b** were prepared according to the reported literature procedure¹ with slight modification.[†] The reactions were performed under normal atmospheric conditions unless otherwise mentioned. Solvents were dried and freshly distilled prior to use. Melting points were recorded on a Veego VMP-I melting point apparatus. ¹H NMR spectra were recorded on Varian VXR 400S, Bruker AMX 500 and on Bruker AV800 spectrometer at frequencies 399.59 MHz, 499.85 and 800 MHz respectively. ¹³C (100.45 MHz) and ¹²⁵Te (157.79 MHz) NMR spectra were recorded on a Varian VXR 400S and Bruker AMX 500 spectrometer respectively. Tetramethylsilyl (SiMe₄) was used as internal standard for ¹H-NMR. Dimethyltelluride was used as external reference for ¹²⁵Te NMR. FT-IR spectra were recorded as KBr pellets on a Nicolet Impact 400 FTIR spectrometer. Elemental analysis was performed on Carlo Erba model 1106 elemental analyzer. The Electro-spray mass spectra were obtained from Thermo Quest Finnigan LCQDECA, ESI-MS (ion trap) mass spectrometer.

[†] **Caution:** Preparation of precursors **3a** and **3b** involves use of mercurated azobenzene derivative. The reactions involving mercury compounds were carried out in a well ventilated fume hood with proper precaution due to their hazardous nature.

Synthesis of phenyltellurinic anhydride: The reaction was performed in the similar manner as for **4**. The white colour powder obtained appeared to be phenyl tellurinic anhydride upon general spectroscopic characterization and elemental analysis. The yield of the compound obtained was 0.16 g, 70%. Mp = 215-218 °C; FT-IR (KBr): 3418 (O-H)^{*}, 3406 (C-H), 1434 (C=C, bend), 733 (C-H, asym), 704 (Te=O), 691 (C-H, bend), 665 (C-H, sym), 642 (Te-O) cm⁻¹. ¹H-NMR (800 MHz, CD₃COOD, 25 °C): δ 8.04 (br, 4H), 7.55 (br, 6H). ¹³C NMR (400 MHz, CD₃COOD, 25 °C): δ 147.05, 132.64, 131.72, 130.11. ¹²⁵Te NMR (500 MHz, CD₃COOD + DMSO (1:3), 25 °C)^ε: δ 965.7 ppm. ESI-MS, m/z 448.9 [C₁₂H₁₀OTe₂Na]⁺, 694.9 [C₁₈H₁₅O₅Te₃]⁺, 904 [C₂₄H₁₉O₄Te₄Na]⁺. Anal. calcd for C₁₂H₁₀O₃Te₂: C, 31.51; H, 2.20. Found: C, 31.29; H, 2.04.

X-ray Crystallography: X-ray diffraction data were obtained on an Oxford Gemini system using Mo-Kα radiation (λ = 0.71073 Å). The structure solutions were achieved by

using direct methods as implemented in SHELXS-97.² The structures were refined by full least-squares methods using SHELXL-97.³

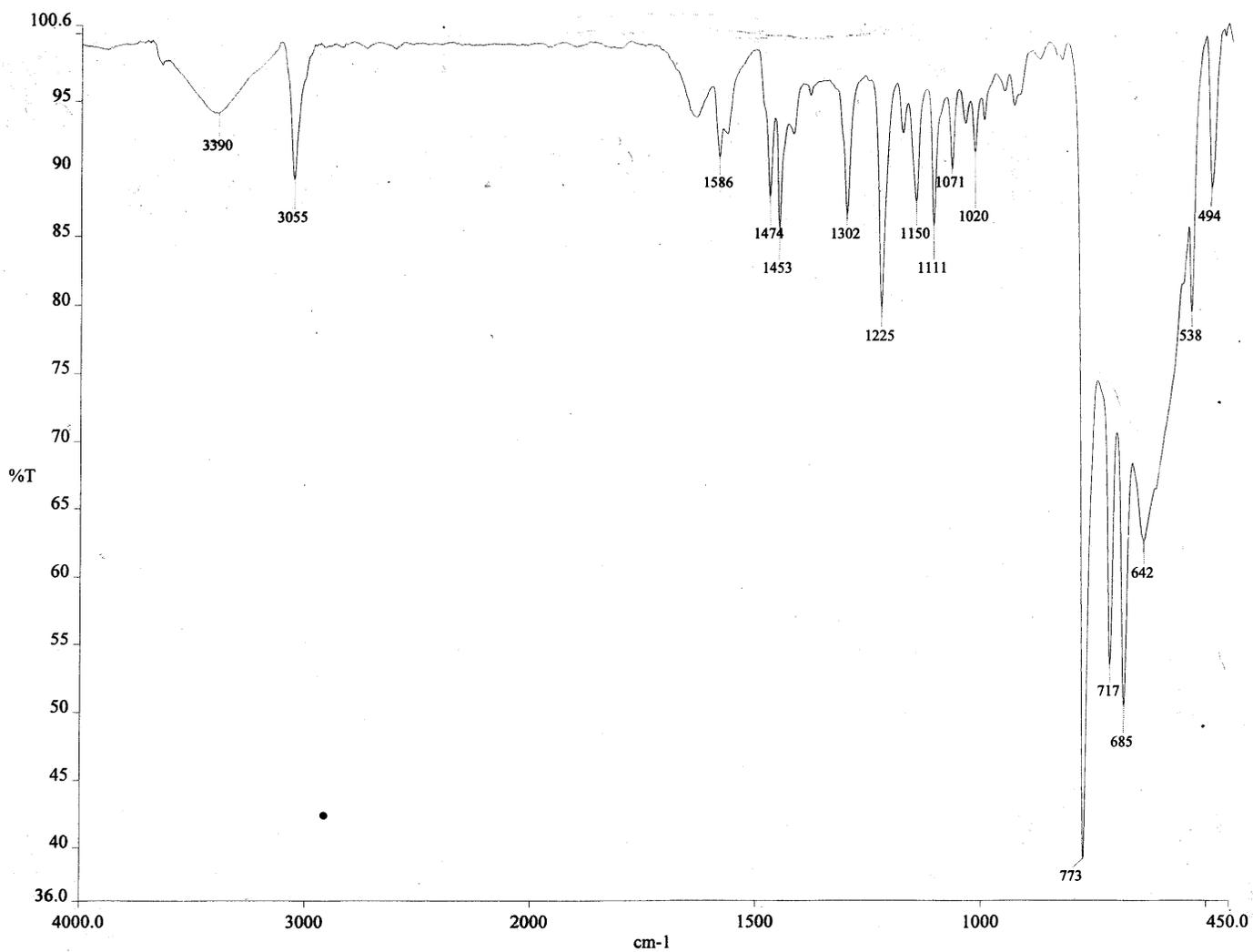


Figure S1. FT-IR spectrum of 4.

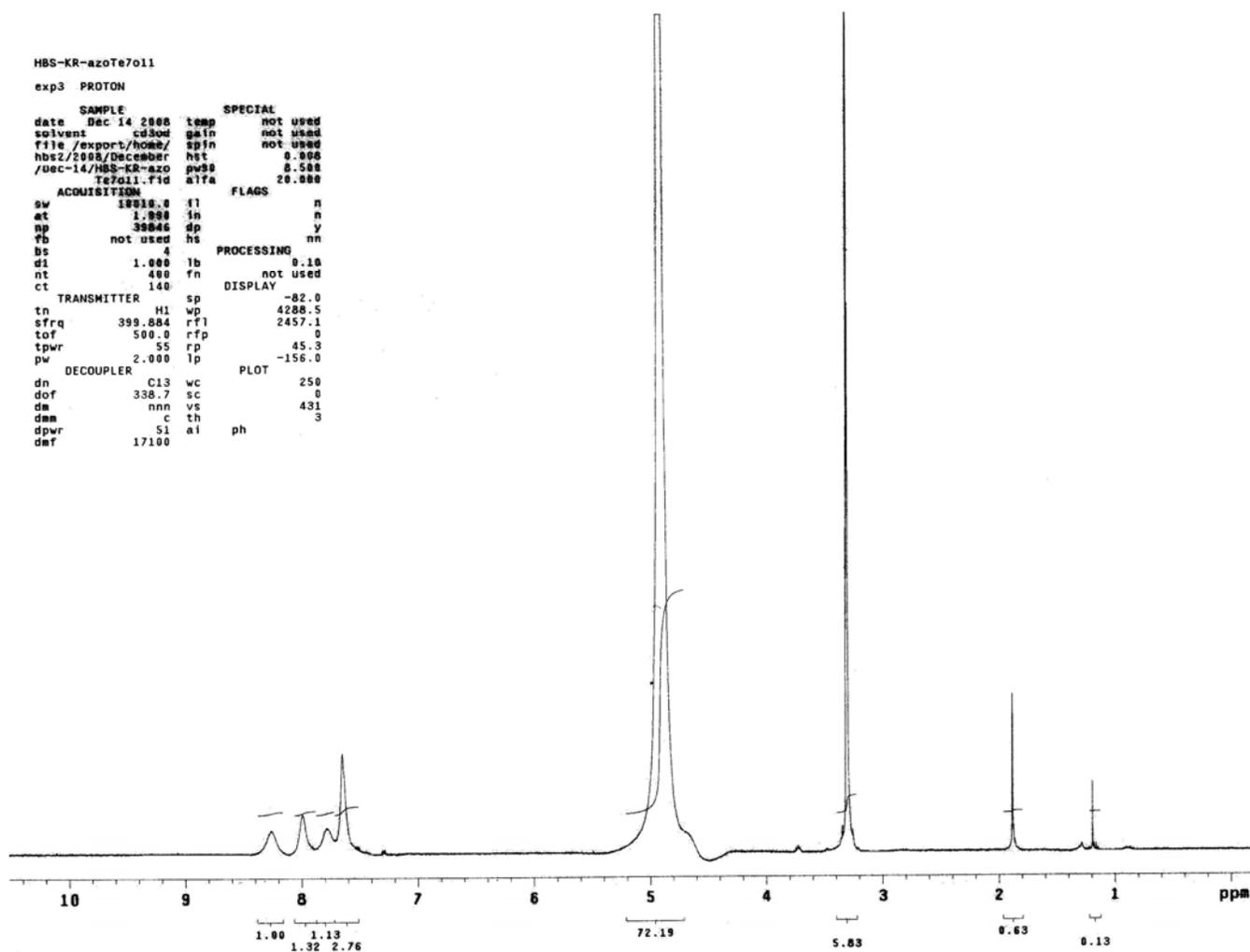


Figure S2. ^1H NMR spectrum of **4** at 25 °C.

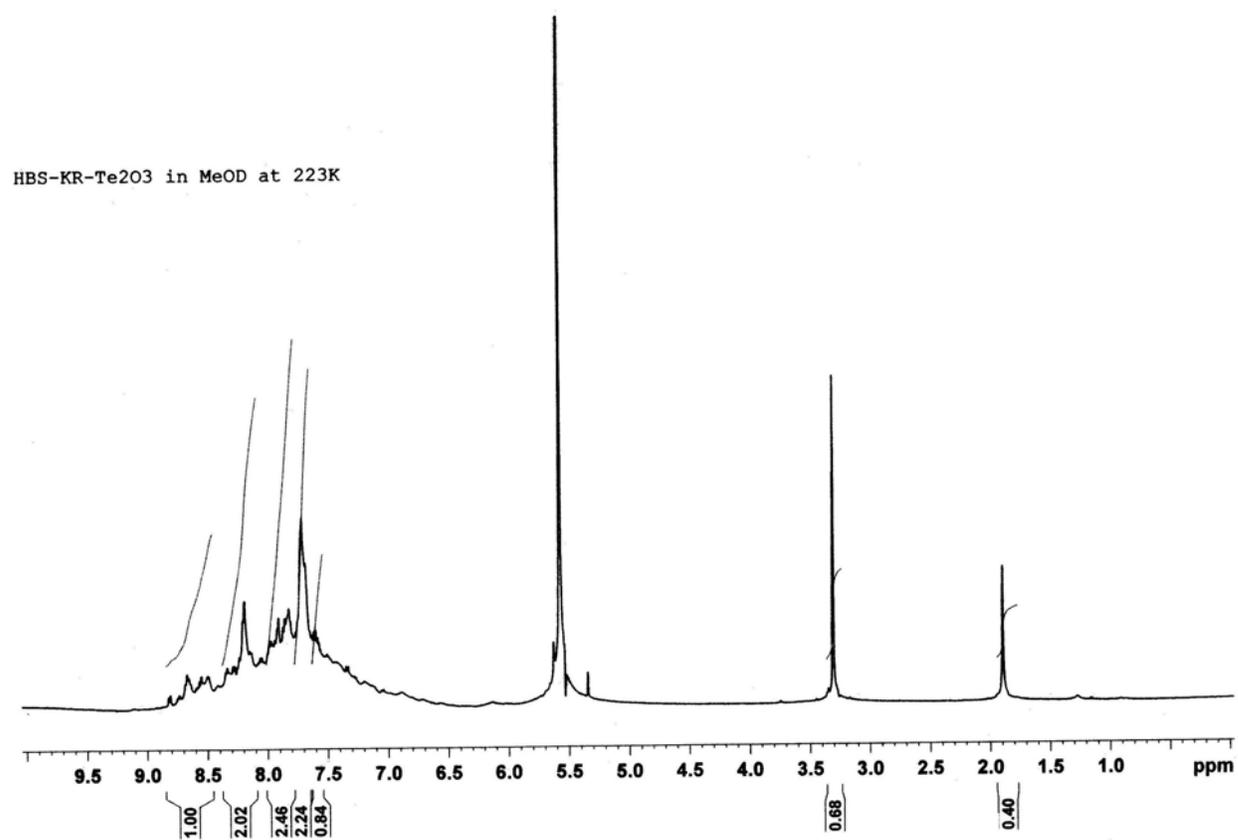


Figure S3. ^1H NMR spectrum of **4** at $-50\text{ }^\circ\text{C}$.

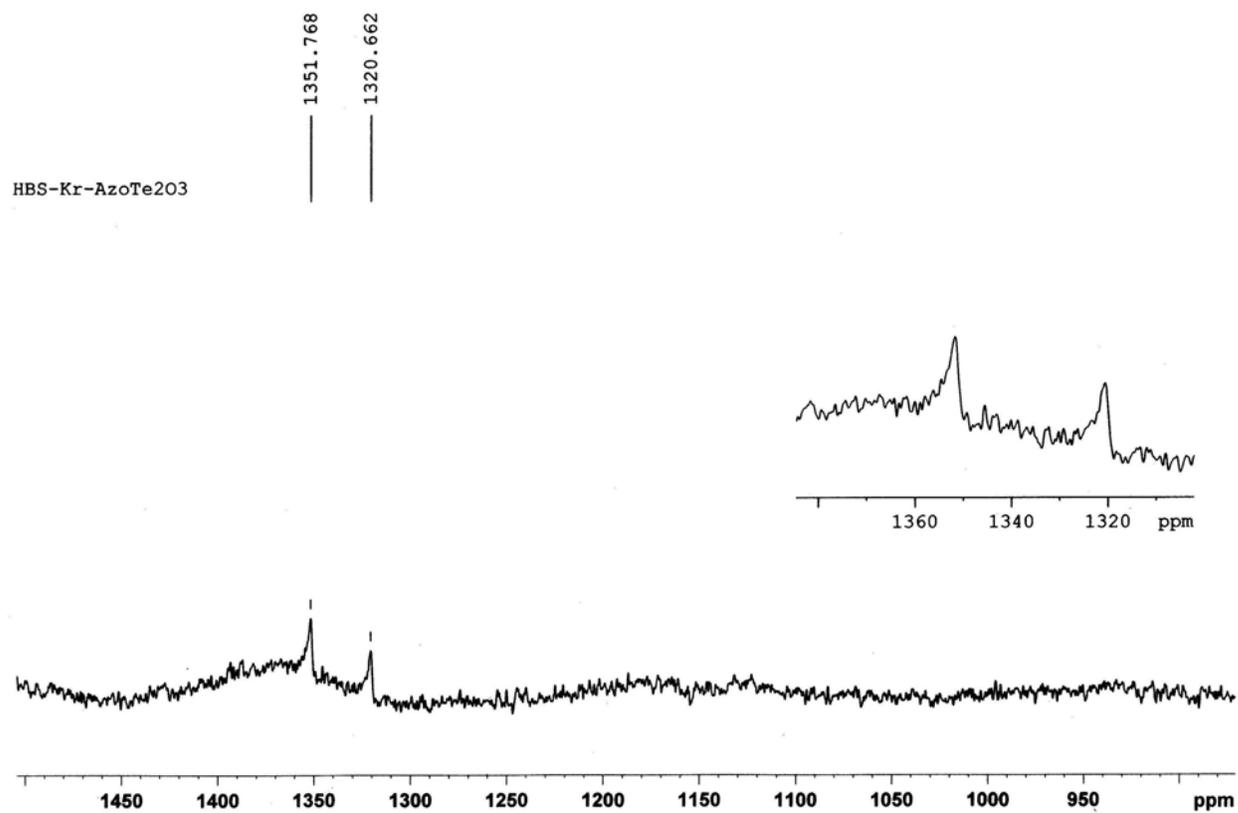


Figure S4. ^{125}Te NMR spectrum of **4** (data acquisition for 29 h)

Eager 300 Report

Page: 1 Sample: HBS-KR-TE203 (HBS-KR-TE203)

Method Name : sp191208
Method File : D:\CHNS2008\sp191208.mth
Chromatogram : HBS-KR-TE203
Operator ID : SP Company Name : C.E. Instruments
Analysed : 12/19/2008 15:01 Printed : 12/19/2008 16:52
Sample ID : HBS-KR-TE203 (# 29) Instrument N. : Instrument #1
Analysis Type : UnkNown (Area) Sample weight : 1.421

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	7.5178	43	115355	RS	13.052280	.107983E+07
Carbon	39.7447	66	1505646	RS	1.000000	.266121E+07
Hydrogen	2.4085	172	237411	RS	6.341938	.660009E+07
Totals	49.6710		1858412			

Figure S6. Elemental analysis (C, H, N) of 4

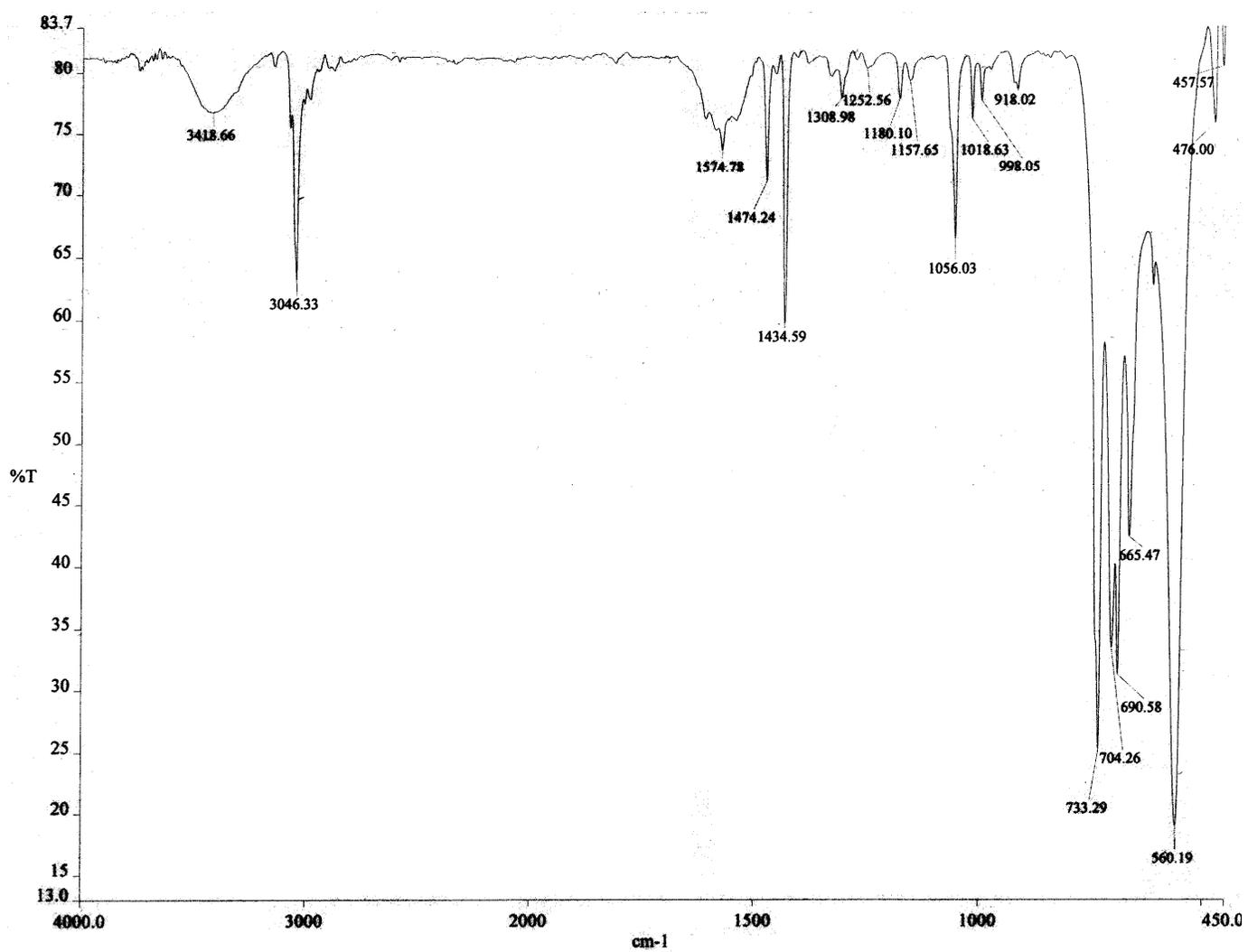
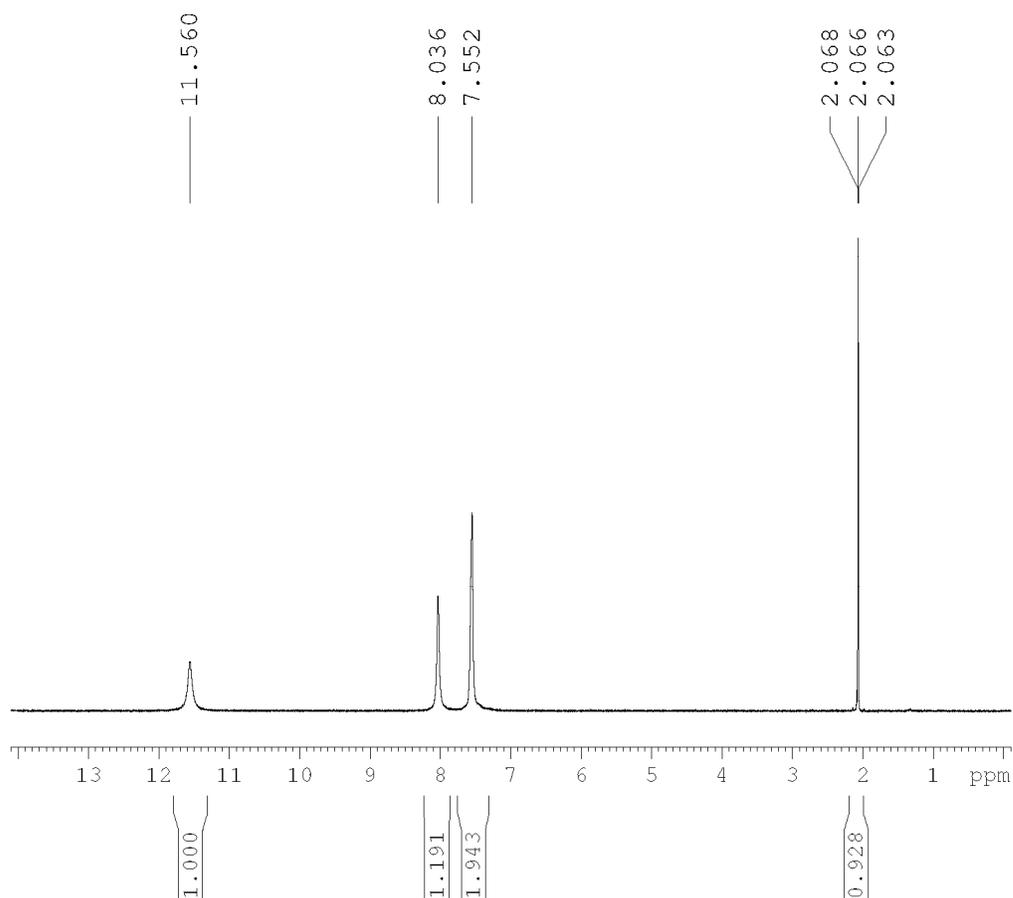


Figure S7. FT-IR spectrum of Ph₂Te₂O₃

sample_PhTe2O3
in d4_acetic_acid



Current Data Parameters
NAME guest_test
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090918
Time_ 23.56
INSTRUM av800
PROBHD 5 mm CPTCI 1H-
PULPROG zg
TD 16384
SOLVENT Acetic
NS 4
DS 0
SWH 11363.637 Hz
FIDRES 0.693581 Hz
AQ 0.7209460 sec
RG 1
DW 44.000 usec
DE 6.00 usec
TE 298.0 K
D1 4.00000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 1.00 usec
PL1 2.30 dB
SFO1 800.2356016 MHz

F2 - Processing parameters
SI 65536
SF 800.2300000 MHz
WDW SINE
SSB 3
LB 0.00 Hz
GB 0
PC 1.00

Figure S8. ^1H NMR spectrum of $\text{Ph}_2\text{Te}_2\text{O}_3$ (In CD_3COOD)

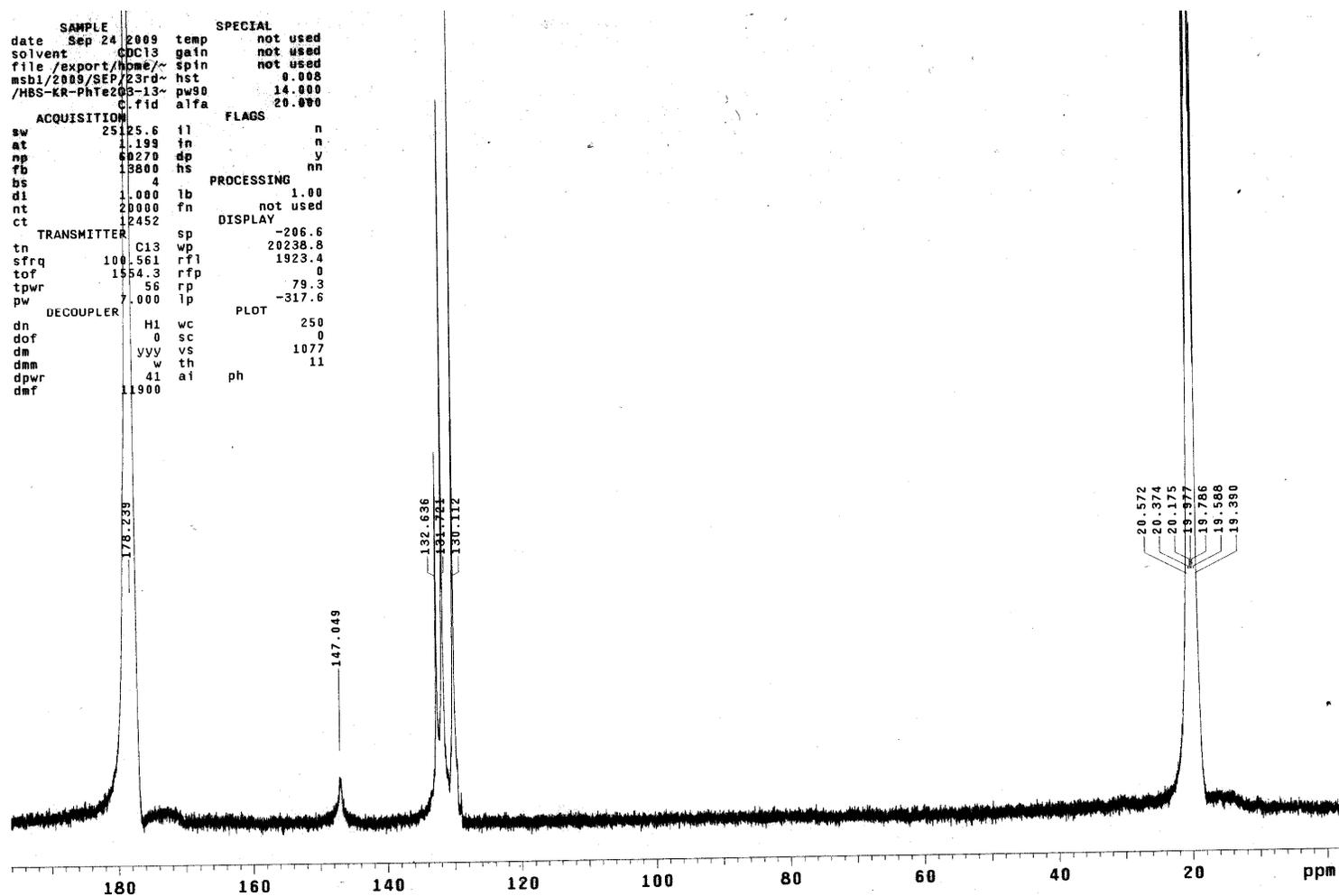


Figure S9. ^{13}C NMR spectrum of $\text{Ph}_2\text{Te}_2\text{O}_3$ (In CD_3COOD)

HBS KR
PHTe203 in acetic acid/DMSO

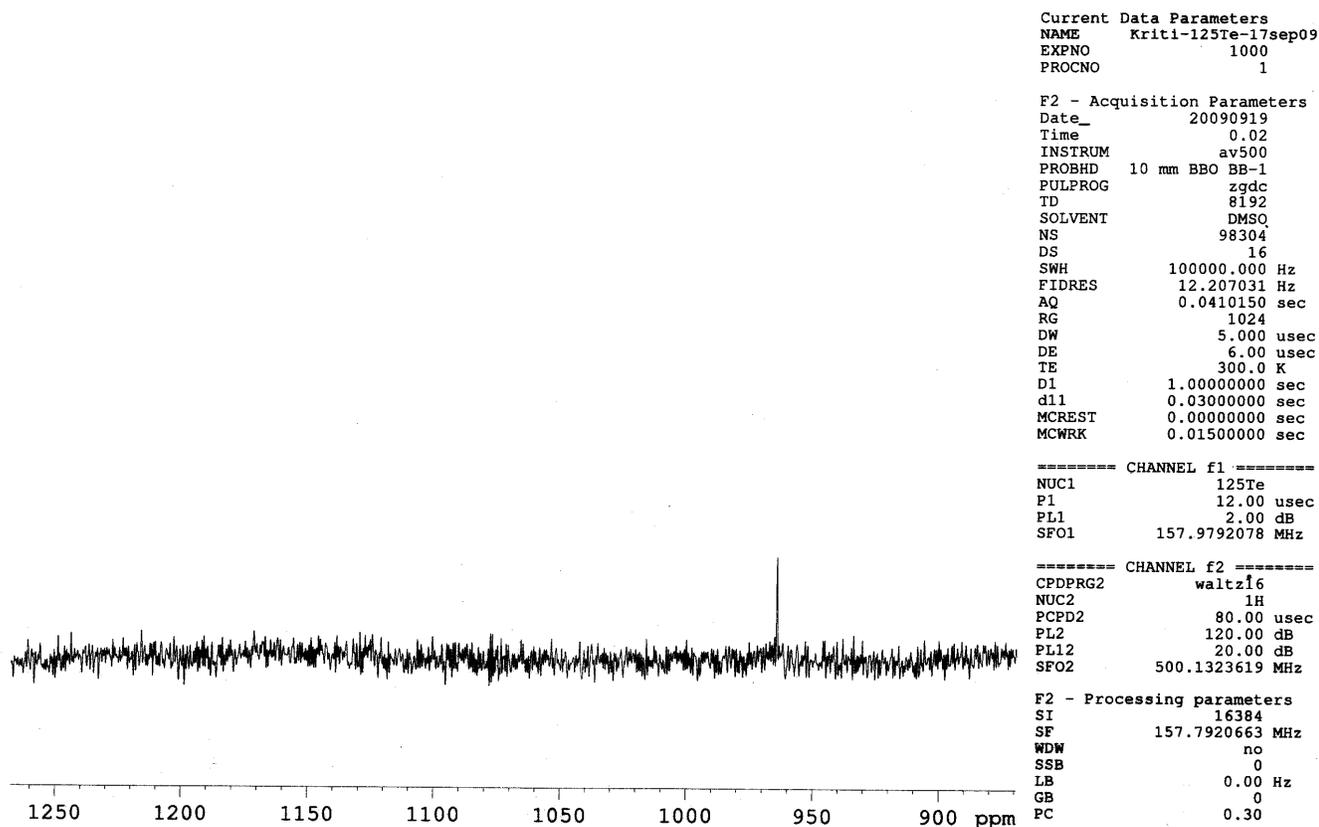


Figure S10. ^{125}Te NMR spectrum of $\text{Ph}_2\text{Te}_2\text{O}_3$ (Due to expensive CD_3COOD , ^{125}Te NMR was recorded in mixture of CD_3COOD and DMSO in 1: 3 ratio)[€]

D:\External_Users\...HBS_KR_01_Neg
BTK1_Tune_300903 3uL T: 250
HBS_KR_01_Neg #1-20 RT: 0.01-0.27 AV: 20 NL: 2.20E5
T: - p Full ms [300.00-1000.00]

09/29/2009 01:04:31 PM

PlaTe2O3

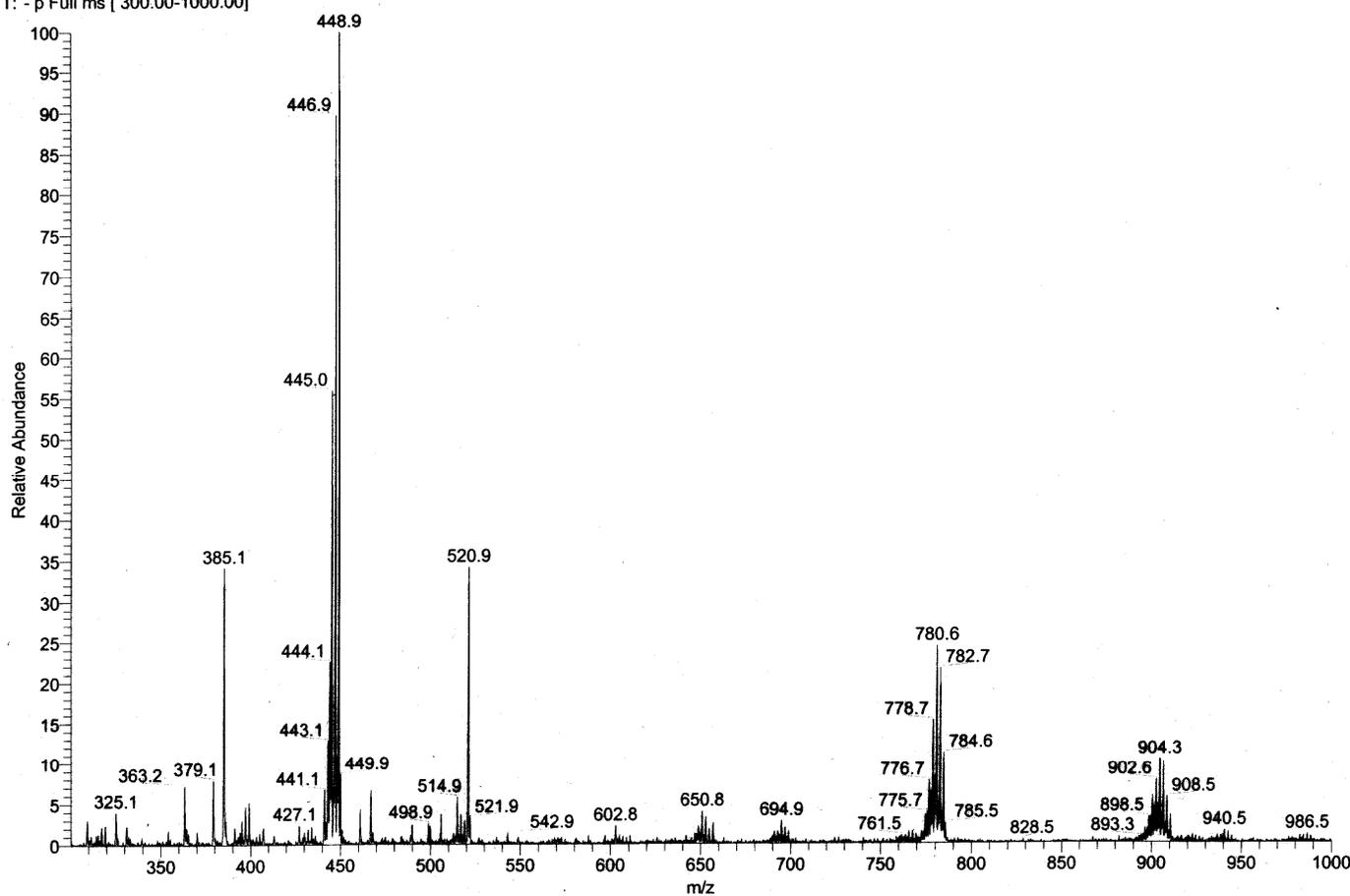


Figure S11. ESI-MS spectrum of $\text{Ph}_2\text{Te}_2\text{O}_3$

Eager 300 Report

Page: 1 Sample: KRTEPH (KRTEPH)

Method Name : SP080909
Method File : D:\CHNS2008\SP080909.mth
Chromatogram : KRTEPH
Operator ID : AGK Company Name : C.E. Instruments
Analysed : 09/08/2009 13:50 Printed : 9/8/2009 14:57
Sample ID : KRTEPH (# 22) Instrument N. : Instrument #1
Analysis Type : UnkNown (Area) Sample weight : 1.293

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Carbon	31.2856	67	997006	RS	1.000000	.246465E+07
Hydrogen	2.0366	175	155178	RS	6.424915	.548662E+07
Totals	33.3222		1152184			

Figure S12. Elemental analysis of $\text{Ph}_2\text{Te}_2\text{O}_3$

Entry	Anionic multi-tellur-oxane^a	Oligotellu- -roxane^b	Polymeric Ditellur- oxane^c	Macrocyclic Multi- Telluranes^d	Tellurinic Acid^e	4
Te-O (short bonds)	1.908- 1.941 (sixteen bonds)	1.890(8) 1.896(8) 1.916(8)			1.897(5)	1.863- 1.891 1.911- 1.913
Te-O (intermediate bonds)		1.964(7)	2.025(2)	1.99(2)- 2.03(2)		1.987- 2.023
Te-O (long bonds)	2.091- 2.157 (sixteen bonds)	2.089(8) 2.116(8)	2.100(2)	2.23(2)- 2.29(2)	2.143(5) and 2.232(4)	2.063- 2.106 2.174- 2.249

Table S1: Comparison of Te-O Bond Lengths of 4 with related Telluroxanes

^a H. Citeau, K. Kirschbaum, O. Conrad and D. M. Giolando, *Chem. Commun.*, 2001, 2006-2007.

^b K. Kobayashi, N. Deguchi, O. Takahashi, K. Tanaka, E. Horn, O. Kikuchi and N. Furukawa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1638-1640.

^c J. Beckmann, D. Dakternieks, A. Duthie, F. Ribot, M. Schürmann and N. A. Lewcenko, *Organometallics*, 2003, **22**, 3257-3261.

^d K. Kobayashi, H. Izawa, K. Yamaguchi, E. Horn and N. Furukawa, *Chem. Commun.*, 2001, 1428-1429.

^e J. Beckmann, P. Finke, M. Hesse and B. Wellig, *Angew. Chem., Int. Ed.*, 2008, **47**, 9982-9984.

References:

1. (a) Z. Majeed, W. R. McWhinnie and T. A. Hamor, *J. Organomet. Chem.*, 1997, **549**, 257-262; (b) R. E. Cobbleddick, F. W. B. Einstein, W. R. McWhinnie and F. H. Musa, *J. Chem. Res. (M)*., 1979, 1901-1909.
2. G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany), 1997.
3. G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany), 1997.