

## An Unusual Binary Phosphorus–Tellurium Anion and Its Seleno- and Thio-Analogues: $P_4Ch_2^{2-}$ (Ch = S, Se, Te)

Christiane Rotter, Michael Schuster, and Konstantin Karaghiosoff\*

Department of Chemistry and Biochemistry, Ludwig-Maximilian University of Munich, Butenandstr. 5-13(D), D-81377 Munich, Germany

Received June 15, 2009

We present an unusual discrete P–Te anion,  $P_4Te_2^{2-}$ , which is readily obtained by the oxidation of white phosphorus with  $Te_2^{2-}$  in *N*-methyl imidazole at ambient temperature. According to the  $^{31}P$  and  $^{125}Te$  NMR spectra, the anion  $P_4Te_2^{2-}$  had a bicyclo-[1.1.0]tetraphosphane (“butterfly”) structure with the tellurium atoms in the exo positions. The anion was remarkably stable at ambient temperature and disproportionated only slowly with the formation of elemental tellurium.  $P_4Te_2^{2-}$  is the first P–Te anion with a bicyclo[1.1.0]tetraphosphane structure. When  $Se_2^{2-}$  or  $S_2^{2-}$  was reacted with white phosphorus, the analogous seleno- and thiophosphate anions  $P_4Se_2^{2-}$  and  $P_4S_2^{2-}$  were formed, thus completing the series of phosphorus–chalcogen anions  $P_4Ch_2^{2-}$  (Ch = S, Se, Te). The synthesis of  $P_4Te_2^{2-}$  demonstrated that binary P–Te anions do exist as stable species in solution.

only one example has been described in the literature. Mewis et al. found in crystalline  $BaP_4Te_2$  the polymeric anion  $(P_4Te_2^{2-})_x$ , which consists of chains of  $P_6$  rings in the chair conformation with the tellurium atoms covalently bonded to phosphorus in the 1,4 position.<sup>8</sup> Here, we report the synthesis and multinuclear ( $^{31}P$ ,  $^{125}Te$ ) NMR spectroscopic characterization of the new anion  $P_4Te_2^{2-}$ , which represents formally the “monomer” of the polymeric  $(P_4Te_2^{2-})_x$  and which is, to our knowledge, the first discrete P–Te anion ever observed. In addition, the synthesis and NMR spectroscopic characterization of the analogous sulfur and selenium phosphorus anions  $P_4Se_2^{2-}$  and  $P_4S_2^{2-}$  are presented.

The increasing interest in metal chalcogenophosphates with the heavier chalcogens sulfur and selenium, due to their interesting material properties like ion conductivity or optoelectrical properties, stimulates the search for new and, in particular, phosphorus-rich chalcogenophosphate anions.<sup>9</sup> The classical syntheses of metal chalcogenophosphates are mainly the domain of solid-state chemistry. They involve reactions at high temperatures in the melt, under hydrothermal conditions, or using polychalcogenide fluxes.<sup>2–5</sup> Our synthetic strategy<sup>6</sup> uses reactions in solution at ambient temperature or below, thus making the formation of metastable chalcogenophosphate anions possible. In particular, P–Te anions, which suffer from the weak phosphorus–tellurium bond, should become accessible under these conditions. Chivers et al. have demonstrated that an anionic tellurium atom bonded to a phosphorus atom stabilizes the phosphorus–tellurium bond, thus preventing tellurium elimination.<sup>10,11</sup> In this context, we investigated the reaction of white phosphorus with  $Na_2Te_2$ ,  $Na_2Se_2$ , and  $Na_2S_2$  in *N*-methyl imidazole at ambient temperature. The reaction with 1.5 equivalents of  $Na_2Te_2$  is completed within 12 h, yielding a dark purple solution. According to the  $^{31}P$  NMR spectrum, the anion  $P_4Te_2^{2-}$  (**1**) is formed almost quantitatively (98%; Scheme 1)

Oxophosphates,  $P_nO_m^{x-}$ , are well-known, extensively investigated, and represent an integral part of every textbook of inorganic chemistry.<sup>1</sup> In contrast, binary phosphorus chalcogen anions,  $P_nCh_m^{x-}$ , with the heavier chalcogens Ch = S, Se, and Te are less common. Indeed, only a limited number of thiophosphate anions,  $P_nS_m^{x-}$ , and only a few selenophosphate anions,  $P_nSe_m^{x-}$ , have been described in the literature so far.<sup>2–6</sup> Interestingly, the known representatives comprise mainly chalcogen-rich ( $n > m$ ) anions, except  $P_7S_3^-$ , which was reported by Baudler and Floruss and characterized in solution using  $^{31}P$  NMR spectroscopy.<sup>7</sup> In the case of tellurophosphate anions,

\*To whom correspondence should be addressed. E-mail: klk@cup.uni-muenchen.de.

(1) Holleman, A.; Wiberg, E.; Wiberg, N. *Lehrbuch der anorganischen Chemie*, 102nd ed.; Walter de Gruyter Verlag: Berlin, 2007.

(2) Chung, I.; Malliakas, C. D.; Jang, J. I.; Canlas, C. G.; Weliky, D. P.; Kanatzidis, M. G. *J. Am. Chem. Soc.*, **2007**, *129* (48), 14996–15006 and references cited therein.

(3) Klinging, W.; Ott, R.; Hahn, H. Z. *Anorg. Allg. Chem.* **1973**, *396*, 271–278.

(4) Krause, W.; Falius, H. Z. *Anorg. Allg. Chem.* **1983**, *496*, 80–93.

(5) Chan, B. C.; Hess, R. F.; Feng, P. L.; Abney, K. D.; Dorhout, P. K. *Inorg. Chem.* **2005**, *44*, 2106–2113 and references cited therein.

(6) Rotter, C.; Schuster, M.; Kidik, M.; Schön, O.; Klapötke, T. M.; Karaghiosoff, K. *Inorg. Chem.* **2008**, *47* (5), 1663–1673 and references cited therein.

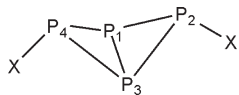
(7) Baudler, M.; Floruss, A. Z. *Anorg. Allg. Chem.* **1994**, *620*, 2070–2076.

(8) Mewis, A.; Jörgens, S.; Johrendt, D. *Chem.—Eur. J.* **2003**, *9*, 2405–2410.

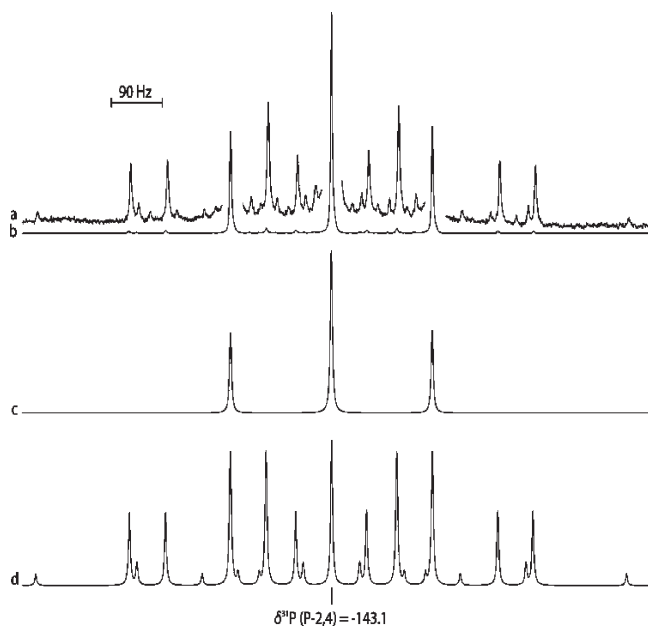
(9) Davies, R. Chalcogen-Phosphorus (and Heavier Congeners) Chemistry. In *Handbook of Chalcogen Chemistry*; Devillanova, F. A., Ed.; RSC Publishing: London, 2007; pp 286–343.

(10) Briand, G. G.; Chivers, T.; Parvez, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3468–3470.

(11) Chivers, T.; Eisler, D. J.; Ritch, J. S. *Dalton Trans.* **2005**, 2675–2677.

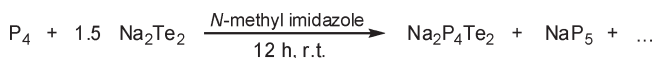


**Figure 1.** Structure of  $P_4Ch_2^{2-}$  (Ch = S, Se, Te). **1**, X =  $Te^-$ ; **2**, X =  $Se^-$ ; **3**, X =  $S^-$ ; **4**, X = Cl; **5**, X = Br; **6**, X =  $SiMe_3$ ; **7**, X =  $N(SiMe_3)_2$ .



**Figure 2.**  $^{31}P$  NMR spectrum of  $P_4Te_2^{2-}$  (**1**). Signal of P2(4), A part of  $AA'M_2X$ : (a) enlarged satellite pattern of the observed spectrum, (b) observed spectrum in *N*-methyl imidazole, (c) calculated<sup>14</sup> spectrum for the isotopomer without NMR-active tellurium (86.2%), (d) calculated spectrum for the isotopomer with one  $^{125}Te$  nucleus (6.6%).

#### Scheme 1. Synthesis of $P_4Te_2^{2-}$



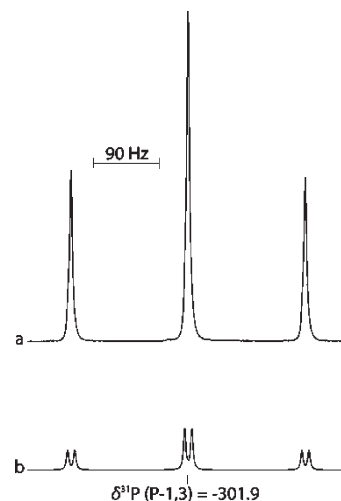
together with traces (2%) of  $P_5^-$  ( $\delta^{31}P = 471^{12}$ ). No other phosphorus-containing species are observed in the solution.

The stoichiometry (1:1.5) as well as the solvent seem to be essential. With less  $Na_2Te_2$ , additional phosphorus-containing products are formed. In less basic solvents, than *N*-methyl imidazole, for example, pyridine, only broad  $^{31}P$  NMR signals are observed. The anion  $P_4Te_2^{2-}$  is remarkably stable in *N*-methyl imidazole solution: it can be kept for 1 day in daylight at ambient temperature or for 4 days at 0 °C without detectable decomposition. After a longer period of time, however, the signals of **1** disappear and new broad signals are observed in the  $^{31}P$  and  $^{125}Te$  NMR spectra, most probably due to anions with still higher phosphorus content.

The analogous reaction of  $P_4$  with  $Na_2Se_2$  yields a complex mixture of P–Se anions, which contains only 30% of the corresponding P–Se anion  $P_4Se_2^{2-}$  (**2**). Among the other products, the anions  $PSe_4^{3-}$ ,  $P_2Se_6^{4-}$ ,  $HPSe_3^{2-}$ ,  $HP_2Se_5^{3-}$ , and  $P_{21}^{3-}$  were identified by  $^{31}P$  and  $^{77}Se$  NMR spectroscopy.<sup>13</sup> When  $Na_2S_2$  is used, only traces (4%) of the P–S anion  $P_4S_2^{2-}$  (**3**) are observed in the reaction solution. The  $^{31}P$

(12) Baudler, M.; Düster, D.; Ouzounis, D. *Z. Anorg. Allg. Chem.* **1987**, *544*, 87–94.

(13) Rotter, C.; Schuster, M.; Klapötke, T. M.; Karaghiosoff, K. Manuscript in preparation.



**Figure 3.**  $^{31}P$  NMR spectrum of  $P_4Te_2^{2-}$  (**1**). Signal of P1(3), M part of the  $AA'M_2X$ : (a) observed spectrum in *N*-methyl imidazole, (b) calculated<sup>14</sup> spectrum for the isotopomer with one  $^{125}Te$  nucleus.

NMR spectrum indicates the formation of phosphorus-rich thiophosphate anions, the identity of which is currently under investigation. Obviously in the series of anions **1–3**, the phosphorus–tellurium anion **1** seems to be the most stable species under the prevailing reaction conditions.

The  $^{31}P$ ,  $^{77}Se$ , and  $^{125}Te$  NMR spectra reveal for the anions **1–3** a bicyclo[1.1.0]tetraphosphane (*butterfly*) structure with the chalcogen atoms in the sterically more favorable exo positions (Figure 1). The symmetrical bicyclic framework is suggested by the  $^{31}P$  NMR spectra of the  $A_2M_2$  type and, in the cases of **1** (Figure 2) and **2**, is further supported by the satellite pattern for the signal of P-2(4), caused by the isotopomer with one magnetically active chalcogen nucleus (A part of the  $AA'M_2X$  spectrum). From the satellite pattern, a large and positive value for the “hidden” coupling constant  $^2J_{PP}$  between the isochronous nuclei P2 and P4 is determined (Table 1), in accord with the exo position of the chalcogen nuclei. No signals corresponding to an exo–endo or endo–endo isomer of **1–3** can be detected in the  $^{31}P$  NMR spectra (Figure 3). The  $^{125}Te$  NMR spectrum of **1** (Figure 4) displays the line pattern for the X part of an  $AA'X$  spectrum; each of the five lines expected for the X part of  $AA'X$  is further split according to first order in a triplet by coupling with the two magnetically equivalent M nuclei. The  $^2J_{TeP}$  coupling (11 Hz) is small, and for P1(3), the  $^{125}Te$  satellites overlap with the main signals (Figure 3).

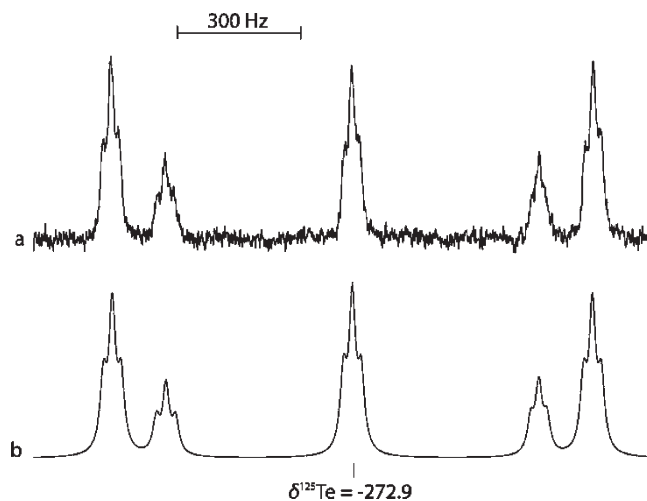
The  $^{31}P$  NMR data of the new anions **1–3** fit well to those of other bicyclo[1.1.0]tetraphosphanes (Table 1). With decreasing electronegativity of the chalcogen, the  $^{31}P$  NMR signals shift to higher field, and the value of  $^1J_{PP}$  decreases. The coupling constants  $^1J_{TeP}$  and  $^1J_{SeP}$  in **1** and **2** are, with values of  $-457$  Hz and  $-336$  Hz, in the expected range and provide rare examples of one-bond couplings of trivalent three-coordinated phosphorus with one coordinated anionic selenium and tellurium, respectively.<sup>18</sup>  $^3J_{TeP}$  in **1** and  $^3J_{SeP}$  in **2** are, with values of  $-138$  Hz and  $-51$  Hz, remarkably large.

(14) Laatikainen, R.; Niemitz, M.; Weber, U.; Sundelin, T.; Hasinen, T.; Vepsäläinen, J. *J. Magn. Reson., A* **1996**, *120*, 1–10.

(15) Tattershall, B. W.; Kendall, N. L. *Polyhedron* **1994**, *13*(10), 1517–1521.

(16) Cappello, V.; Baumgartner, J.; Dransfeld, A.; Flock, M.; Hassler, K. *Eur. J. Inorg. Chem.* **2006**, 2393–2405.

(17) Niecke, E.; Rieger, R.; Krebs, B. *Angew. Chem.* **1982**, *94*(7), 553–554.



**Figure 4.**  $^{125}\text{Te}$  NMR spectrum of  $\text{P}_4\text{Te}_2^{2-}$  (**1**). X part of  $\text{AA}'\text{M}_2\text{X}$ : (a) observed spectrum in *N*-methyl imidazole, (b) calculated<sup>14</sup> spectrum.

A bicyclo[1.1.0]tetraphosphane has been postulated as a reaction intermediate for the nucleophilic degradation of white phosphorus<sup>19,20</sup> and has been shown to be the initial product of the oxidation of white phosphorus with  $\text{Cl}_2$  and  $\text{Br}_2$ .<sup>15</sup> The formation of the new binary anions **1–3** implies the oxidative addition of the isoelectronic dichalcogenides  $\text{Te}_2^{2-}$ ,  $\text{Se}_2^{2-}$ , and  $\text{S}_2^{2-}$  to one of the P–P bonds in the  $\text{P}_4$  tetrahedron and fits well into this picture.

With the synthesis of the first discrete P–Te anion  $\text{P}_4\text{Te}_2^{2-}$  (**1**) and its full characterization by  $^{31}\text{P}$  and  $^{125}\text{Te}$  NMR spectroscopy, described here, we have demonstrated that binary phosphorus tellurium anions can exist as stable species in solution. The results suggest the possible existence of further phosphorus-rich P–Te anions. Together

(18) Karaghiosoff, K. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; Wiley: Chichester, U.K., 1996; Vol. 6, pp 3612–3619.

(19) Brown, C.; Hudson, R. F.; Wartew, G. A. *Phosphorus Sulfur* **1978**, *5*, 67–80.

(20) Baudler, M.; Adamek, C.; Opiela, S.; Budzikiewicz, H.; Ouzounis, D. *Angew. Chem.* **1988**, *100*, 1110–1111.

(21) Boudjouk, P.; Thompson, D. P. *J. Org. Chem.* **1988**, *53*, 2109–2112.

**Table 1.** NMR Chemical Shifts and Coupling Constants of New (**1–3**) and Literature-Known (**4–8**) Bicyclo[1.1.0]tetraphosphanes

		$\delta$ [ppm]		$J$ [Hz]
<b>1</b> <sup>a</sup> (X = Te <sup>−</sup> )	P-2,4	−143.1	<sup>1</sup> $J_{\text{PP}}$	−180
	P-1,3	−301.9	<sup>2</sup> $J_{\text{P}2\text{P}4}$	168
	Te	−272.9	<sup>1</sup> $J_{\text{TeP}2(4)}$	−457
			<sup>2</sup> $J_{\text{TeP}1(3)}$	11
		<sup>3</sup> $J_{\text{TeP}2(4)}$	−138	
<b>2</b> <sup>a</sup> (X = Se <sup>−</sup> )	P-2,4	−90.5	<sup>1</sup> $J_{\text{PP}}$	−206
	P-1,3	−284.0	<sup>2</sup> $J_{\text{P}2\text{P}4}$	181
	Se	−160.0	<sup>1</sup> $J_{\text{SeP}2(4)}$	−336
			<sup>2</sup> $J_{\text{SeP}1(3)}$	< 8
		<sup>3</sup> $J_{\text{SeP}2(4)}$	−51	
<b>3</b> (X = S <sup>−</sup> )	P-2,4	−64.9	<sup>1</sup> $J_{\text{PP}}$	−222
	P-1,3	−271.6		
<b>4</b> <sup>15</sup> (X = Cl)	P-2,4	−54.5	<sup>1</sup> $J_{\text{PP}}$	−215
	P-1,3	−290.4		
<b>5</b> <sup>15</sup> (X = Br)	P-2,4	−72.7	<sup>1</sup> $J_{\text{PP}}$	−203
	P-1,3	−294.4		
<b>6</b> <sup>16</sup> (X = SiMe <sub>3</sub> )	P-2,4	−155.0	<sup>1</sup> $J_{\text{PP}}$	162
	P-1,3	−329.2		
<b>7</b> <sup>17</sup> (X = N(SiMe <sub>3</sub> ) <sub>2</sub> )	P-2,4	−79.1	<sup>1</sup> $J_{\text{PP}}$	222
	P-1,3	−287.3		

<sup>a</sup> The signs of the coupling constants result from the iterative fitting of the NMR spectra assuming a negative sign for  $^1J_{\text{PP}}$ ,  $^1J_{\text{TeP}}$ , and  $^1J_{\text{SeP}}$ .<sup>18</sup>

with the anions  $\text{P}_4\text{Se}_2^{2-}$  (**2**) and  $\text{P}_4\text{S}_2^{2-}$  (**3**), the synthesis and NMR spectroscopic characterization of which have been presented here for the first time, we introduce a new type of phosphorus-rich binary phosphorus–chalcogen anions with a bicyclo[1.1.0]tetraphosphane structure. Further investigations on the synthesis and characterization of phosphorus-rich seleno- and tellurophosphate anions are in progress.

**Acknowledgment.** Financial support from the Department of Chemistry and Biochemistry, Ludwig-Maximilian University of Munich, is gratefully acknowledged. We thank Prof. Thomas M. Klapötke for many helpful discussions and for his continuous support.

**Supporting Information Available:** The general procedure associated with compounds **1**, **2**, and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.