

## Chemistry of Phosphorus Selenide Anions: Synthesis and Structure of $P_2Se_8^{2-}$ and $[Fe_2(CO)_4(PSe_5)_2]^{2-}$

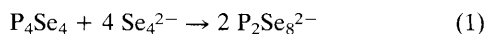
Jin Zhao, William T. Pennington and Joseph W. Kolis\*

Department of Chemistry, Clemson University, Clemson SC 29634, USA

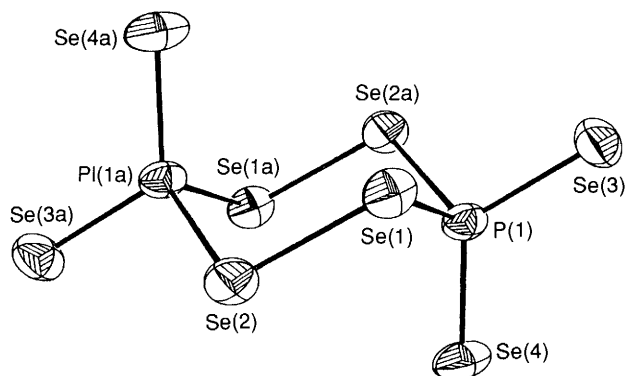
Reaction of  $P_4Se_4$  with soluble polyselenides generates the first isolated phosphorus selenide anion,  $P_2Se_8^{2-}$ , which further reacts with an excess of  $Fe(CO)_5$  to generate the novel cluster  $[Fe_2(CO)_4(PSe_5)_2]^{2-}$ , which has been characterized by crystallography.

In contrast to that of the phosphates, the chemistry of anionic phosphorus sulfides and selenides is not well developed.<sup>1</sup> Most previous work has focused on neutral cages of sulfur<sup>2,3</sup> and selenium,<sup>4-6</sup> though some work with anionic sulfides hints at the presence of a very rich chemistry.<sup>7</sup> We are currently investigating the anionic selenides of phosphorus, arsenic and antimony. Of particular interest are their reactions with transition-metal complexes, since the transition metals have shown a tendency to stabilize a variety of hitherto unknown main-group fragments.<sup>8</sup> We have developed several synthetic entries to these compounds, but one which has shown enormous potential is the reaction of anionic main-group clusters with metal carbonyls.<sup>9</sup> In this communication we report a convenient preparation of the first phosphorus selenide anionic cluster and its reaction with  $Fe(CO)_5$  to form a unique cluster which contains the novel  $PSe_5^{3-}$  fragment.

The binary phosphorus selenide anion  $P_2Se_8^{2-}$  can be prepared from the nucleophilic degradation of  $P_4Se_4$  glass by excess soluble polyselenide anion in dimethylformamide (DMF), [eqn. (1)]. The anion can be readily isolated as its



[ $PPh_4$ ]<sup>+</sup> salt.<sup>†</sup> It has been characterized by analytical and

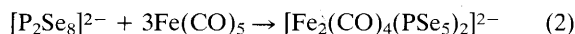


**Fig. 1** Thermal ellipsoid (50% probability) plot of  $[P_2Se_8]^{2-}$ ; selected bond distances (Å): Se(1)–Se(2) 2.338(2), P(1)–Se(1) 2.276(2), P(1)–Se(2) 2.282(3), P(1)–Se(3) 2.139(3), P(1)–Se(4) 2.102(3); selected angles (°): Se(1)–P(1)–Se(2a) 103.6(1), Se(1)–P(1)–Se(3) 99.9(1), Se(1)–P(1)–Se(4) 114.2(2), Se(2a)–P(1)–Se(4) 112.7(1)

<sup>†</sup> *Synthetic and spectroscopic data:* All reactions were performed under argon using standard Schlenk techniques. The salt  $[PPh_4]_2[P_2Se_8]$  was prepared by combining  $P_4Se_4$  (0.11 g) and  $K_2Se_4$  (0.32 g) in DMF (10 ml) and stirring for 2 h until the colour turned clear light green. A DMF solution (5 ml) containing  $[PPh_4]Br$  (0.25 g) was added and the solution filtered. Slow addition of diethyl ether and storage overnight at 4 °C produced a yellow crystalline product (0.282 g, 47% yield). The complex  $[PPh_4]_2[Fe_2(CO)_4(PSe_5)_2]$  was made by preparing a clear green phosphorus selenide solution as described above, and treating it with  $Fe(CO)_5$  (0.15 ml) added *via* syringe. The solution was stirred for 4 h and to it  $[PPh_4]Br$  (0.25 g in 5 ml DMF) was added *via* syringe. The brown solution was filtered and layered with diethyl ether (10 ml) and stored overnight at 40 °C leading to formation of brown crystals (0.512 g, 36% yield) of the product. IR (CO) 1990 and 1938  $cm^{-1}$ . A test reaction, using pre-made  $[PPh_4]_2[P_2Se_8]$  crystals as starting material, also gave the complex but in somewhat lower yield. Both new compounds gave satisfactory elemental analysis.

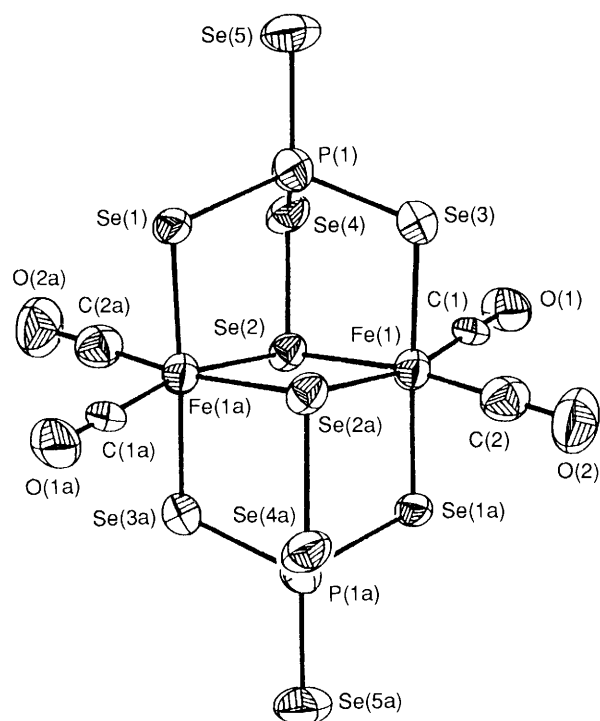
physical methods including single crystal X-ray diffraction.<sup>‡</sup> Its structure consists of a six-membered  $P_2Se_4$  ring with each phosphorus atom containing two terminal selenide atoms (see Fig. 1), formally placing each phosphorus atom in the  $P^V$  state. The ring P–Se distances are approximately 0.15 Å longer than the terminal P–Se distances, as would be expected.<sup>5,6</sup> The six-membered ring is in the chair conformation with the phosphorus atoms *para* relative to each other, and the overall structure is nearly identical with the corresponding  $P_2S_8^{2-}$  prepared by nucleophilic degradation of  $P_4S_{10}$ .<sup>10</sup> The <sup>31</sup>P NMR spectrum displays a singlet at  $\delta -5.57$  with <sup>1</sup> $J_{P-Se}$  satellites with couplings of 298 and 667 Hz, with the larger coupling assigned to the terminal phosphorus selenides due to the shorter P–Se distance and increased double-bond character.

The  $P_2Se_8^{2-}$  anion reacts with an excess of  $Fe(CO)_5$  to form the novel cluster  $[Fe_2(CO)_4(PSe_5)_2]^{2-}$  in reasonable yield [eqn. (2)]. The cluster contains two iron dicarbonyl fragments



bridged by a selenium atom from two  $PSe_5$  groups (see Fig. 2). The terminal P–Se bond is short like those in the parent dianion at 2.144(5) Å, while the other P–Se distances are somewhat longer [average 2.22(1) Å], though still slightly shorter than those in the uncomplexed ring. The Se–Se distance is typical at 2.373(5) Å and the angles around the phosphorus atoms are very close to ideal tetrahedral. With the  $Fe \cdots Fe$  distance greater than 3.6 Å, there is no interaction between the metal atoms. The Fe–Se distances range from 2.409(4) to 2.477(4) Å. These distances are somewhat long for bridging selenides<sup>11</sup> but typical for non-bridging iron–selenide rings.<sup>12</sup> The coordination environment around each iron is only slightly distorted from octahedral. The <sup>31</sup>P NMR is again informative, with a singlet at  $\delta 4.29$  possessing three <sup>77</sup>Se

<sup>‡</sup> *Crystallographic data:*  $[PPh_4]_2[P_2Se_8]$ ,  $M = 1372.42$ , triclinic, space group  $P\bar{1}$ ,  $a = 9.845(2)$ ,  $b = 10.689(2)$ ,  $c = 12.570(2)$  Å,  $\alpha = 95.58(1)$ ,  $\beta = 97.21(2)$ ,  $\gamma = 109.40(2)^\circ$ ,  $V = 1224.0(4)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 1.862$  g  $cm^{-3}$ ,  $R = 0.0649$  for 2956 observed [ $I > 3\sigma(I)$ ] reflections.  $[PPh_4]_2[Fe_2(CO)_4(PSe_5)_2]$ ,  $M = 1754.07$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.207(2)$ ,  $b = 11.151(2)$ ,  $c = 13.271(3)$  Å,  $\alpha = 81.46(1)$ ,  $\beta = 76.03(2)$ ,  $\gamma = 79.78(2)^\circ$ ,  $V = 1433.7(5)$  Å<sup>3</sup>,  $Z = 1$ ,  $D_c = 2.032$  g  $cm^{-3}$ ,  $R = 0.0597$  for 2093 observed [ $I > 3\sigma(I)$ ] reflections. All measurements were made on a Nicolet R3m V diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The data were collected at a temperature of  $21 \pm 1$  °C, using an  $\omega$ –2 $\theta$  scan technique to a  $2\theta$  value of 48.0° for  $[PPh_4]_2[P_2Se_8]$  and 45.0° for  $[PPh_4]_2[Fe_2(CO)_4(PSe_5)_2]$ . An empirical absorption correction, based on azimuthal scans for six reflections, was applied. The data were corrected for Lorentz and polarization effects, and the structures solved by direct methods. In both cases, the midpoint of the anion coincided with a crystallographic centre of symmetry. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were included as a riding model in calculated positions with a refined isotropic group thermal parameter. Approximately 10% [ $m = 0.094(2)$ ] of the anion sites for  $[PPh_4]_2[Fe_2(CO)_4(PSe_5)_2]$  were occupied by a disordered alternate anion  $[Fe_2(CO)_4(PSe_4)_2]^{2-}$  (see supplementary material). All calculations were performed using the SHELXTL+ crystallographic package of programs. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Fig. 2** Thermal ellipsoid (50% probability) plot of  $[\text{Fe}_2(\text{CO})_4(\text{PSe}_5)_2]^{2-}$ ; significant bond distances (Å): P(1)–Se(1) 2.214(6), P(1)–Se(3) 2.216(6), P(1)–Se(4) 2.240(6), P(1)–Se(5) 2.143(5), Se(2)–Se(4) 2.371(3), Fe(1)–Se(1a) 2.409(4), Fe(1)–Se(2) 2.477(4), Fe(1)–Se(2a) 2.460(4), Fe(1)–Se(3) 2.472(3); selected angles (°): Se(1)–P(1)–Se(5) 111.1(1), Se(4)–P(1)–Se(5) 110.3(2), Fe(1)–Se(2)–Fe(1a) 94.0(1), Se(2)–Fe(1)–Se(2a) 86.0(1), Se(1a)–Fe(1)–Se(2) 86.2(1), Se(1)–Fe(1a)–Se(3a) 175.4(2)

satellites with coupling values of 377, 484 and 676 Hz, of intensity ratios 1:2:1. These can be assigned as the P–Se(4), P–Se(1) [Se(3)] and P–Se(5) couplings, respectively.

To our knowledge, this is the first reported example of any group 15/16 fragment with this shape. We have previously reported a tungsten phosphorus selenide complex of formula  $[\text{Se}=\text{W}(\text{PSe}_4)(\text{PSe}_2)]^{2-}$ ,<sup>8</sup> but it does not contain a phosphorus selenide group like that reported here. We have also prepared

Mo and W complexes containing coordinated  $\text{AsSe}_5$  groups,<sup>13</sup> but they have a different shape owing to the reluctance of arsenic to assume the  $\text{As}^{\text{V}}$  oxidation state. Each  $\text{PSe}_5$  group in the iron complex can be assigned as having a formal 3– charge with one terminal selenide having no formal charge and the remaining terminal selenides bearing negative formal charges. This places a formal charge of 2+ on each of the iron atoms. With each ligand donating two electrons, the iron atoms have a complete 18 electron count. Thus, this compound is another example of an oxidative decarbonylation reaction, where an anionic main-group cage oxidatively adds to a low-valent transition-metal centre leading to further cluster build-up.

We are indebted to the National Science Foundation (CHE-9102548) and the Alfred P. Sloan Foundation for support of this work.

Received, 7th November 1991; Com. 1/05679D

## References

- 1 D. E. C. Corbridge, *Phosphorus An Outline of its Chemistry Biochemistry and Technology*, Elsevier Science Publishing, New York, 4th edn., 1990.
- 2 D. B. Sowerby, *The Chemistry of Inorganic Homo- and Heterocycles*, ed. I. Haiduc and D. B. Sowerby, Academic Press, London, 1987.
- 3 H. Hoffmann and M. Becke-Goehring *Top. Phosphorus Chem.*, 1976, **8**, 193.
- 4 R. Blachnik, H.-P. Baldus, P. Lonnecke and B. W. Tattershall, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 605.
- 5 J. D. Fitzmaurice, D. J. Williams, P. T. Wood and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1988, 741.
- 6 S. W. Hall, M. J. Pilkington, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Polyhedron*, 1991, **10**, 261.
- 7 See for example, H. Falius, W. Krause and W. S. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 103.
- 8 S. C. O'Neal, W. T. Pennington and J. W. Kolis, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1486.
- 9 J. W. Kolis, *Coord. Chem. Rev.*, 1990, **105**, 195.
- 10 P. C. Mishall and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1978, **34**, 1378.
- 11 C. F. Campana, F. Y.-K. Lo and L. F. Dahl, *Inorg. Chem.*, 1979, **18**, 3060.
- 12 H. Strasdeit, B. Krebs and G. Henkel, *Inorg. Chim. Acta*, 1984, **89**, L11.
- 13 S. C. O'Neal, W. T. Pennington and J. W. Kolis, *J. Am. Chem. Soc.*, 1991, **113**, 710.