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An extended network of twenty-membered $K_6Se_6P_4N_4$ rings: X-ray structure of $\{[(THF)K[Bu^tN(Se)P(\mu\text{-}NBu^t)_2P(Se)NBu^t]K(THF)_2]_2\}_\infty$

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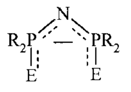
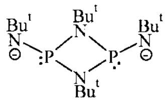
The partially THF-solvated dipotassium salt of the novel bis-chelating dianion $[Bu^tN(Se)P(\mu\text{-}NBu^t)_2P(Se)NBu^t]^{2-}$ forms an infinite network of twenty-membered $K_6Se_6P_4N_4$ rings involving two types of K···Se interactions.

The coordination chemistry of monoanions of the type $[R_2P(E)NP(E)R_2]^-$ **1** is a very active area of investigation.[1] The interest in metal complexes of these acetylacetonate analogues includes their use in catalysis[2] or as lanthanide shift reagents,[3] as well as the stabilization of unusual geometries at main group metal centres.[4] The dianionic bis(amido) P(III) ligand **2** has also been studied recently for possible applications in catalysis[5] and as a ligand for main group metals.[6] Bischalcogenido derivatives of **2** are unknown. Such dianionic P(V) ligands **3** would be especially interesting in view of the possibility of (a) selective chelation of different metals *via* S,S′ or Se,Se′ (soft) and N,N′ (hard) centres or (b) generation of metal-containing polymers *via* bis-chelation. Here, we describe the synthesis and X-ray structures of the first alkali metal derivatives of **3a** and **3b**.



1 (E = O, S, Se)



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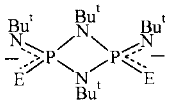
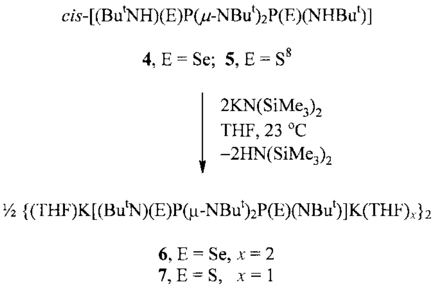


3a, E = Se
3b, E = S

The dianions **3a** and **3b** are obtained as their dipotassium salts **6** and **7** in good yields *via* the deprotonation reaction depicted in Scheme 1.† The ^1H and ^{13}P $\{^1H\}$ NMR spectra of **6** and **7** are consistent with symmetrical bis-chelation of the dianions to two K^+ ions, but these spectroscopic data do not distinguish between two possible bonding modes: (a) bis-(N,E) chelation or (b) N,N′ and E,E′ chelation. The ^{31}P $\{^1H\}$ NMR spectrum of the diprotonated precursor **4** shows two pairs of ^{77}Se satellites attributable to the AA′X spin system of the isotopomer containing one ^{77}Se ($I = \frac{1}{2}$, 7.6%) atom.†[7] The value of $^1J(^{31}P–^{77}Se)$ is reduced from 880 to 684 Hz upon deprotonation consistent with a decrease in P–Se bond order (*cf.* 786 and 687 Hz for $Ph_2P(Se)NHP(Se)Ph_2$ and its K^+ salt).[7] The A–A′ $[^2J(^{31}P–^{31}P)]$ coupling is 25 Hz in **4**, but it is unresolved for **6**. A reliable estimate of the number of THF ligands per K^+ ion by integration of the ^1H NMR spectra of **6** and **7** could not be obtained owing to the facile loss of THF from the crystals.



Scheme 1

The X-ray structural analysis of **6** (Fig. 1)‡ reveals that bis-chelation occurs at the 'top' and 'bottom' of the dianion (Se,Se′ and N,N′) in preference to 'side-on' bis(N,Se) chelation. Presumably the formation of six-membered KNPNPN and KSePNPSe rings is preferred over the known four-membered KNPSe ring[9] for the relatively large K^+ ion. The mean K–Se distance in the monomeric unit is 3.312 Å, *cf.* 3.377 Å for $(K[Ph_2P(Se)NSiMe_3]\cdot THF)_2$.[9] Fig. 2 shows that dimerization occurs *via* two K··Se interactions (3.418(3) Å) to give a central K_2Se_2 ring as observed for $(K[Ph_2P(Se)NSiMe_3]\cdot THF)_2$.[9] For **6**, however, the K^+ ions involved in these four-membered rings are bis-solvated (five-coordinate). The X-ray crystal structure of the sulfur analogue **7** is similar to that of **6** except that both K^+ ions are monosolvated.[10] The dimeric units in **6** associate further *via* weak··Se interactions (3.644(3) Å) involving the monosolvated K^+ ions and the two-coordinate Se atoms to give an extended structure. Extended ladder structures involving K··E interactions have been reported previously for the unsolvated complexes $K[Ph_2P(E)NP(E)Ph_2]$ (E = S,[11a] Se[11b]). For **6** the

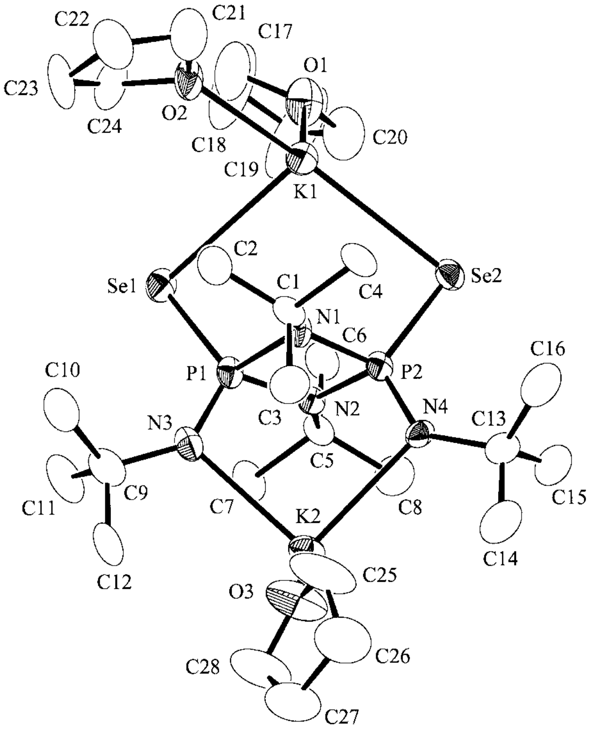


Fig. 1 The X-ray structure of the monomeric unit in **6** showing the numbering scheme. Selected bond lengths (Å) and angles (°): K(1)–Se(1) 3.354(3), K(1)–Se(2) 3.270(4), K(2)–N(3) 2.766(11), K(2)–N(4) 2.804(10), P(1)–Se(1) 2.171(4), P(2)–Se(2) 2.163(4), P(1)–N(3) 1.546(10), P(2)–N(4) 1.552(10), P(1)–N(1) 1.735(9), P(1)–N(2) 1.715(10), P(2)–N(1) 1.717(10), P(2)–N(2) 1.703(8); Se(1)–K(1)–Se(2) 97.14(8), N(3)–K(2)–N(4) 91.2(3), Se(1)–P(1)–N(3) 119.5(4), Se(2)–P(2)–N(4) 119.8(4), P(1)–Se(1)–K(1) 86.66 (11), P(2)–Se(2)–K(1) 87.64(12), P(1)–N(3)–K(2) 105.1(5), P(2)–N(4)–K(2) 104.0(5).

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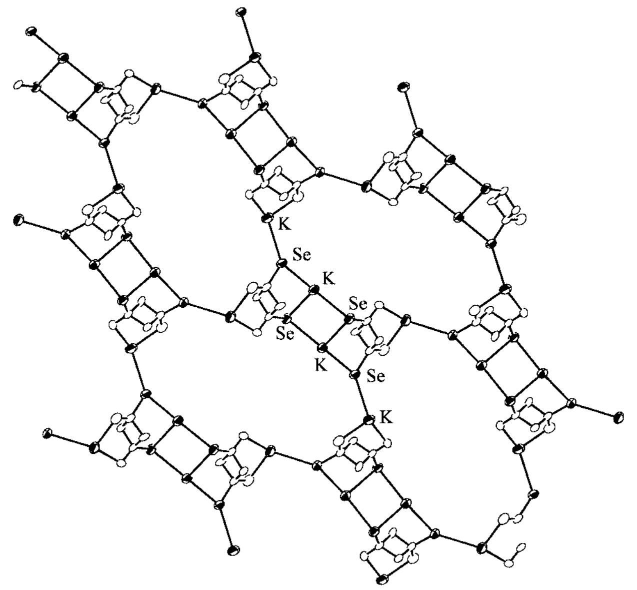

Fig. 2 The extended structure of **6** showing the two types of K··Se interactions. For clarity Bu^t groups and THF are omitted.

presence of two K$^+$ ions per monomeric building block allows the formation of an extended network of twenty-membered ($K_6Se_6P_4N_4$) rings (Fig. 2). The sulfur analogue **7** forms a similar extended structure.[10] By contrast, we note that the sodium salt of **3a**, $(THF)_2Na[Bu^tN(Se)P(\mu\text{-}NBu^t)_2P(Se)(NBu^t)]Na(THF)_2$ **8**, in which *both* Na$^+$ ions are bis-solvated, has a monomeric structure similar to that depicted in Fig. 1.[10] The $^{31}P\{^1H\}$ NMR parameters for **8** in d_8-THF are δ +3.9, $^1J(^{31}P–^{77}Se)$ = 678 Hz and $^2J(^{31}P–^{31}P)$ = 6.1 Hz.

Investigations of the formation of metal-containing coordination polymers involving the novel bis-chelating dianions **3a** and **3b** are in progress. Details of the structural characterization of **7** and **8** will be provided in the full account of this work.

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Notes and references

† *Synthesis* of **6**: *cis*-$[(Bu^tNH)(Se)P(\mu\text{-}NBu^t)_2P(Se)(NHBu^t)]$ **4** was obtained in *ca.* 80% yield from the reaction of $[(Bu^tNH)P(\mu\text{-}NBu^t)P(NHBu^t)]$ with elemental selenium in boiling toluene for 18 h. NMR (d_8-THF): ^1H, δ 4.56 (s, 2H, NH), 1.68 (s, 18H, Bu^t), 1.46 (s, 18H, Bu^t); $^{31}P\{^1H\}$, δ 26.7 (s, $^1J(^{31}P–^{77}Se)$ 880, $^2J(^{31}P–^{31}P)$ 25 Hz; ^{77}Se, δ −128.4 (d, $J(^{31}P–^{77}Se)$ 877 Hz). IR (cm^{-1}): 3383 [ν(N–H)], 581 [ν(PSe)].

A solution of $KN(SiMe_3)_2$ (1.66 g, 7.90 mmol) in THF (10 mL) was added slowly to a stirred solution of **4** (2.00 g, 3.95 mmol) in THF at 23 °C. After 2 h solvent was removed under vacuum and the product was washed with hexane (2 × 10 mL) to give **6** (2.07 g, 2.59 mmol) as a yellow powder. X-Ray quality crystals were obtained from THF–hexane (1:1) solution at 23 °C. NMR (d_8-THF): ^1H, δ 3.58 (m, OCH_2CH_2), 1.74 (m, OCH_2CH_2), 1.66 (s, 18H, Bu^t), 1.33 (s, 18H, Bu^t); $^{31}P\{^1H\}$, δ −0.03 (s, $^1J(^{31}P–^{77}Se)$ 686 Hz); ^{77}Se, δ 13.2 (d, $J(^{31}P–^{77}Se)$ 684 Hz). IR (cm^{-1}): 514 [ν(PSe)].

Synthesis of **7**: complex **7** was obtained in 81% yield as a yellow powder from $KN(SiMe_3)_2$ (5.00 mmol) and **5**[7] (2.50 mmol) in THF (20 mL) by a procedure similar to that described above for **6**. NMR (d_8-THF): ^1H, δ 3.58 (m, OCH_2CH_2), 1.75 (m, OCH_2CH_2), 1.60 (s, 18H, Bu^t), 1.31 (s, 18H, Bu^t); $^{31}P\{^1H\}$, δ 26.6 (s), IR (cm^{-1}): 551 [ν(PS)].

‡ *Crystal data* for **6**: $C_{28}H_{60}N_4K_2O_3P_2Se_2$, *M* = 798.87, monoclinic, space group $P2_1/n$ (no. 14), a = 10.733(11), b = 14.085(10), c = 26.138(9) Å, β = 90.99(5)°, V = 3951(5) Å^3, Z = 4, D_c = 1.343 g cm^{-3}, μ(Mo-Kα) = 21.94 cm^{-1}. Crystal dimensions 0.50 × 0.30 × 0.20 mm. Data were measured on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-Kα radiation using ω scans. The structure was solved by direct methods and refined anisotropically using data that were corrected for absorption. Three carbon atoms of a THF molecule (C18, C19 and C20) had large thermal displacement parameters. 2135 of the 6958 unique reflections has $I \geqslant 2.00\sigma(I)$. The final agreement factors were R = 0.0640, R_w = 0.1652.

CCDC 182/1532. See http://www.rsc.org/suppdata/cc/b0/b000357n/ for crystallographic files in .cif format.

1 For recent reviews, see: J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 2893; I. Haiduc, R. Cea-Olivares, S. Hernandez-Ortega and C. Silvestru, *Polyhedron*, 1995, **14**, 2041.
2 N. Platzer, H. Rudler, C. Alvarez, L. Barkaoui, B. Denise, N. Goasdoue, M. N. Rager, J. Vaissermann and J. C. Daran, *Bull. Chem. Soc. Fr.*, 1995, **132**, 95.
3 H. Rudler, B. Denise, J. R. Gregorio and J. Vaissermann, *Chem. Commun.*, 1997, 2299.
4 R. Cea-Olivares, J. Novosad, J. D. Woollins, A. M. Z. Slawin, V. Garcia-Montalvo, G. Espinosa-Pérez and P. Garcia y Garcia, *Chem. Commun.*, 1996, 519; V. Garcia-Montalvo, J. Novosad, P. Kilian, J. D. Woollins, A. M. Z. Slawin, P. Garcia y Garcia, M. Lopez-Cardoso, G. Espinosa-Pérez and R. Cea-Olivares, *J. Chem. Soc., Dalton Trans.*, 1997, 1029.
5 L. Grocholl, L. Stahl and R. J. Staples, *Chem. Commun.*, 1997, 1465.
6 L. Grocholl, I. Schranz, L. Stahl and R. J. Staples, *Inorg. Chem.*, 1998, **37**, 2496; I. Schranz, L. Stahl and R. J. Staples, *Inorg. Chem.*, 1998, **37**, 1493.
7 P. Bhattacharyya, J. Novosad, J. Phillips, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 1607; P. Bhattacharyya, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 2489.
8 T. G. Hill, R. C. Haltiwanger, M. L. Thompson, S. A. Katz and A. D. Norman, *Inorg. Chem.*, 1994, **33**, 1770.
9 T. Chivers, M. Parvez and M. A. Seay, *Inorg. Chem.*, 1994, **33**, 2147.
10 T. Chivers, M. Krahn and M. Parvez, unpublished results.
11 (*a*) A. M. Z. Slawin, J. Ward, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1994, 421; (*b*) J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1996, 2893.

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