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Synthesis and Crystal Structures of Octahedral Metal Complexes containing the New Dianion $[PhP(Se,O)Se\text{-}Se(O,Se)PPh]^{2-}$

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Dedicated to Professor Michael Binnewies on the Occasion of his 60th Birthday

Abstract. The synthesis and structures of three new compounds are reported. $[Mg_2\{PhP(Se,O)Se\text{-}Se(O,Se)PPh\}_2(thf)_7(H_2O)_3]$ (**1**), $[Mg\{PhP(Se,O)Se\text{-}Se(O,Se)PPh\}(thf)_3(H_2O)]$ (**2**), and $[Mn\{PhP(Se,O)Se\text{-}Se(O,Se)PPh\}(thf)_3(H_2O)]$ (**3**) were prepared by treatment of Woollins' reagent $[PhP(Se)(\mu\text{-}Se)]_2$ with the corresponding hydrated metal acetates.

Keywords: Magnesium; Manganese; Phosphorus; Selenium; Crystal structure

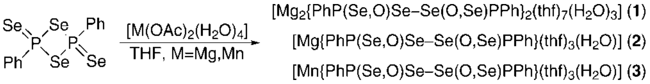
Introduction

The chemistry of metal complexes containing anionic phosphorus/selenium-ligands is currently intensively studied [1−6]. In addition to the great structural diversity observed in this class of compounds, the potential applications of new phosphorus-containing metal selenides in semiconducting devices is of interest [7].

For the revival of this area which was pioneered by *Kuchen* et al. [8], the availability of P−Se-containing starting materials was a key issue. For the present investigations, the synthesis of Woollins' reagent (W. R.) $[PhP(Se)(\mu\text{-}Se)]_2$ [9, 10] (which is commercially available) and its conversion to metal complexes containing P−Se ligands was the starting point for the development of a general route to coordination oligomers, polymers and clusters based on neutral P/Se precursors [11, 12]. The present work follows up results obtained earlier from reactions of neutral P/S and As/S precursors with metal salts [13−17] and describes the first solid-state structures of a new P/Se-anion with divalent metal ions.

Results and Discussion

The reaction of $[PhPSe(\mu\text{-}Se)]_2$ (W. R.) with the hydrated metal carboxylate $[NaOAc{\cdot}3H_2O]$ has recently been reported and it was shown that the presence of water played a crucial role in the formation of the resulting coordination polymer $2/\infty[Na_2(PhPSe_2O)(H_2O)_4(thf)]_\infty$ [11]. As an extension of this initial report, a number of metal carboxylates were reacted with W. R. and herein synthesis and crystal structures of the first examples of metal complexes containing the new dianion $[PhP(Se,O)Se\text{-}Se(O,Se)PPh]^{2-}$ are reported. Out of a number of first-row transition metal and main group metal carboxylates so far only those of magnesium and manganese have led to products which could be characterized unequivocally (Scheme 1).



Scheme 1 Synthesis of **1**-**3**.

1 crystallizes in the orthorhombic space group *P*ca2_1 with two differently-coordinated Mg atoms in the asymmetric unit. The constituting magnesium complexes $[Mg\{PhP(Se,O)Se\text{-}Se(O,Se)PPh\}(thf)_3(H_2O)]$ and $[Mg\{PhP(Se,O)Se\text{-}Se(O,Se)PPh\}(thf)_4(H_2O)_2]$ in **1** exhibit an octahedral metal coordination environment (Fig. 1). The new generated ligand $[PhP(Se,O)Se\text{-}Se(O,Se)PPh]^{2-}$ chelates the magnesium atoms and coordinates in a similar fashion like the neutral related ligand 1,2-*Bis*-diphenylphosphineoxide [18, 19]. The two isolated units are connected by a weak hydrogen bond between Se(5) and O(6) (distance Se5···O6 ca. 3.35 Å) [20]. Other hydrogen bonds present include the strongly bound THF at O(12) and a weak H-bond between Se(1) and O(6). **2** is very similar to **1**. Slightly modified experimental conditions, however have led to a slight change in the substitution pattern of the magnesium atom in $[Mg\{PhP(Se,O)Se\text{-}Se(O,Se)PPh\}(thf)_3(H_2O)]$ (**2**) (Fig. 2).

2 crystallizes in the monoclinic space group *P*2_1/c with two crystallographically independent molecules in the asymmetric unit. Attempts to characterize the new anion spectroscopically were also made and indicated that **2** slowly decomposes in $[D_6]$DMSO. It was, however, possible to dissolve **2** by stirring crystals in $[D_8]$THF during 12 hours. In the $^{31}P\{^1H\}$NMR a singlet resonance for the

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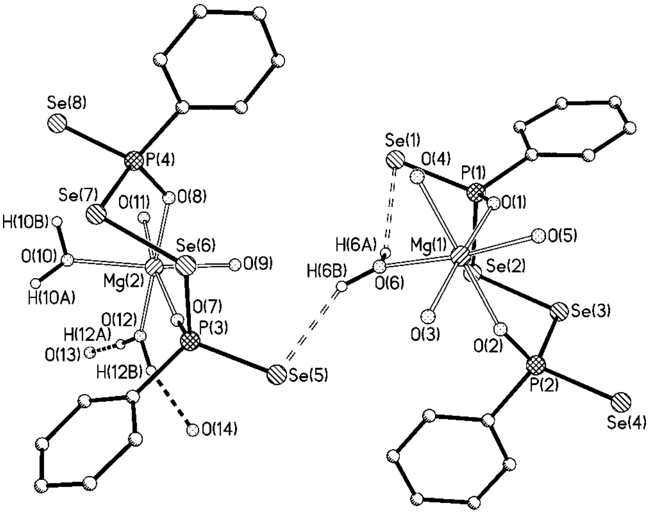

Figure 1 Molecular structure of **1** in the solid state [carbon atoms of THF at O(3, 4, 5, 9, 11, 13, 14) have been omitted for clarity]. Selected bond lengths /Å and angles /°:

Se(1)-P(1) 2.113(2), Se(2)-P(1) 2.261(2), Se(3)-P(2) 2.249(2), Se(4)-P(2) 2.124(2), Se(5)-P(3) 2.131(2), Se(6)-P(3) 2.250(2), Se(7)-P(4) 2.252(2), Se(8)-P(4) 2.121(2), Se(2)-Se(3) 2.3302(12), Se(6)-Se(7) 2.3360(12), P(1)-O(1) 1.503(5), P(2)-O(2) 1.499(5), P(3)-O(7) 1.493(6), P(4)-O(8) 1.485(6), Mg(1)-O(1) 2.008(6), Mg(1)-O(2) 1.986(6), Mg(2)-O(8) 2.025(6), Mg(2)-O(7) 2.036(6), Mg-O(3, 4, 5, 9, 11; thf) 2.089(6)-2.151(6), Mg-O(H_2O) 2.057(6)-2.091(6), Se(5)···O(6) ca. 3.35, Se(1)···O(6) ca. 3.43, O(12)···O(13) ca. 2.68, O(12)···O(14) ca. 2.69, P(1)-Se(2)-Se(3) 99.35(6), P(2)-Se(3)-Se(2) 99.62(6), P(3)-Se(6)-Se(7) 103.44(6), P(4)-Se(7)-Se(6) 100.38(6), O(1)-P(1)-Se(1) 118.2(2), O(1)-P(1)-Se(2) 110.3(2), Se(1)-P(1)-Se(2) 101.40(8), O(2)-P(2)-Se(4) 119.3(2), O(2)-P(2)-Se(3) 110.4(2), Se(4)-P(2)-Se(3) 102.20(8), O(7)-P(3)-Se(5) 120.3(2), O(7)-P(3)-Se(6) 113.0(2), Se(5)-P(3)-Se(6) 98.27(8), O(8)-P(4)-Se(8) 118.3(2), O(8)-P(4)-Se(7) 111.1(2), Se(8)-P(4)-Se(7) 100.99(9), O(2)-Mg(1)-O(1) 93.7(2), O(8)-Mg(2)-O(7) 91.5(2).

[PhP(Se,O)Se-Se(O,Se)PPh]$^{2-}$ dianion was observed together with two satellite sets, which can be ascribed to $^{1}J_{\text{P-Se}}$ coupling to chemically inequivalent terminal and 'inner' Se atoms [2, 12]. In the ^{77}Se NMR spectra of **1** and **2**, however, one weak resonance at ca. 40 ppm was detected, whilst at 131 ppm a further resonance could be ascribed to the different Se environments present. Generally, NMR investigations are complicated by low solubility of **1** and **2**.

The incorporation of paramagnetic metal ions into the new ligand framework was finally exemplified by treating W. R. with [Mn(OAc)$_2$(H$_2$O)$_4$] and X-ray analysis of crystals of **3** (Figure 3).

3 crystallizes in the monoclinic space group $P2_1/c$ with two crystallographically independent, but chemically equivalent [Mn{PhP(Se,O)Se-Se(O,Se)PPh}(thf)$_3$(H$_2$O)] (**3**) complexes in the asymmetric unit. In the extended solid-state structure **3** forms a 1D polymeric arrangement held together by weak hydrogen bonds (Se1···O12A ca. 3.36 Å). The formation of the [PhP(Se,O)Se-Se(O,Se)PPh]$^{2-}$ in **1-3** represents a new development in P-Se chemistry. The new ligand can be regarded as the product of an oxidation of the recently reported [PhP(O)Se$_2$]$^{2-}$ anion [11]. Future work will both attempt to clarify the mechanisms, involved in nucleophilic addition/hydrolysis reactions of neutral P-chalcogen precursors and use the formation of novel ligands for the synthesis of novel coordination polymers.

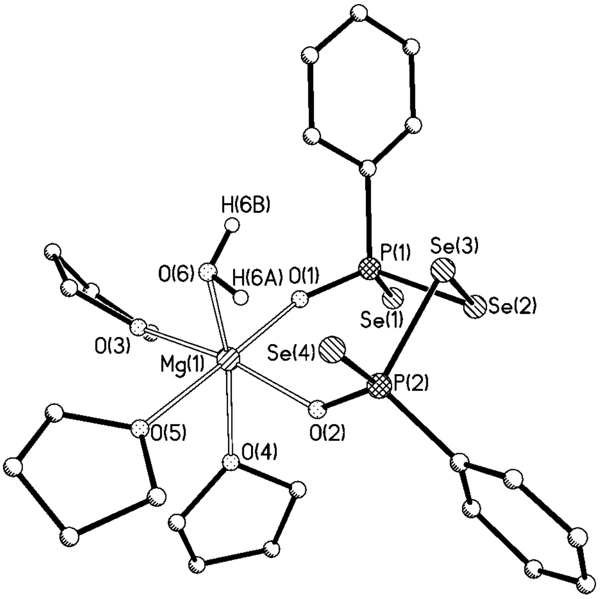

Figure 2 Molecular structure of one of the two complexes present in the asymetric unit of **2** (disordered components of THF ligands are omitted). Selected bond lengths /Å and angles /°:

Se(1)-P(1) 2.127(4), Se(2)-P(1) 2.247(4), Se(2)-Se(3) 2.329(2), Se(3)-P(2) 2.241(4), Se(4)-P(2) 2.134(4), P(1)-O(1) 1.496(10), P(2)-O(2) 1.519(8), Mg(1)-O(1) 1.996(11), Mg(1)-O(2) 2.016(9), Mg(1)-O(3, 4, 5; thf) 2.02(2)-2.190(16), Mg(1)-O(6) 2.090(9), P(1)-Se(2)-Se(3) 98.54(11), P(2)-Se(3)-Se(2) 100.11(11), O(1)-P(1)-Se(1) 118.6(4), O(1)-P(1)-Se(2) 111.0(4), Se(1)-P(1)-Se(2) 102.48(16), O(2)-P(2)-Se(4) 117.8(4), O(2)-P(2)-Se(3) 111.1(4), Se(4)-P(2)-Se(3) 99.73(14), O(1)-Mg(1)-O(2) 93.1(4).

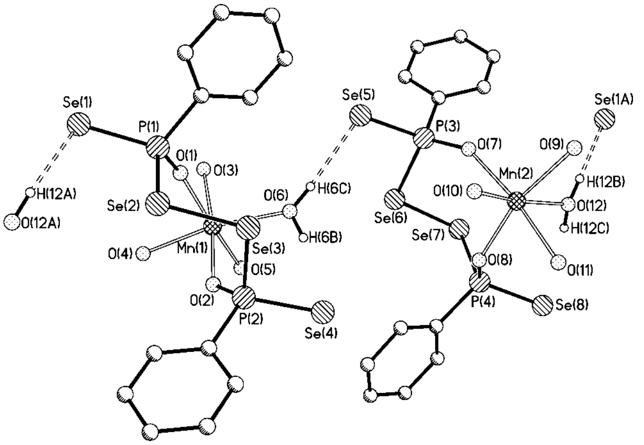

Figure 3 Molecular structure of **3** (connections to adjacent complexes in the 1D polymeric arrangement of complexes are indicated by dashed bonds; symmetry operation (A) x, y+1, z) [carbon atoms of THF at O(3, 4, 5, 9, 10, 11) have been omitted for clarity]. Selected bond lengths /Å and angles /°:

Mn(1)-O(1) 2.078(6), Mn(1)-O(2) 2.124(6), Mn(2)-O(7) 2.138(6), Mn(2)-O(8) 2.096(6), Mn-O(3, 4, 5, 9, 10, 11; thf) 2.188(6)-2.284(6), Mn(1)-O(6) 2.206(6), Mn(2)-O(12) 2.186(7), Se(1)-P(1) 2.124(2), Se(2)-P(1) 2.264(2), Se(2)-Se(3) 2.3353(12), Se(3)-P(2) 2.249(2), Se(4)-P(2) 2.118(2), Se(5)-P(3) 2.125(2), Se(6)-P(3) 2.247(2), Se(6)-Se(7) 2.3306(14), Se(7)-P(4) 2.261(2), Se(8)-P(4) 2.120(2), P(1)-O(1) 1.497(6), P(2)-O(2) 1.517(6), P(3)-O(7) 1.505(6), P(4)-O(8) 1.502(6), Se(1)···O(12A) ca. 3.36, O(1)-Mn(1)-O(2) 95.9(2), O(8)-Mn(2)-O(7) 94.6(2), P(1)-Se(2)-Se(3) 98.71(7), P(2)-Se(3)-Se(2) 102.02(6), P(3)-Se(6)-Se(7) 101.71(7), P(4)-Se(7)-Se(6) 98.46(7), O(1)-P(1)-Se(1) 118.0(3), O(1)-P(1)-Se(2) 110.2(3), Se(1)-P(1)-Se(2) 102.23(9), O(2)-P(2)-Se(4) 118.6(3), O(2)-P(2)-Se(3) 111.4(3), Se(4)-P(2)-Se(3) 99.55(9), O(7)-P(3)-Se(5) 120.8(3), O(7)-P(3)-Se(6) 113.2(3), Se(5)-P(3)-Se(6) 98.13(9), O(8)-P(4)-Se(8) 119.6(3), O(8)-P(4)-Se(7) 109.2(3), Se(8)-P(4)-Se(7) 101.45(9).

Experimental Part

All operations were carried out in an atmosphere of purified dinitrogen. Solvents were dried over appropriate drying agents and freshly distilled.

1: A mixture of 266 mg (0.5 mmol) Woollins' reagent and 107 mg (0.5 mmol) $[Mg(OAc)_2(H_2O)_4]$ was dissolved in 8 mL THF. The yellow solution was heated to 50 °C for 5 hours and then stirred 12 h at room temperature. The reaction was filtered and the filtrate layered with 50 mL hexane. Storage of the solution at room temperature for 4 weeks produced yellow crystals. 0.26 g, yield 60 % (based on $[Mg(OAc)_2(H_2O)_4]$ supplied). mp 130 °C (decomposition); Found: C, 32.79; H, 4.17. $C_{44}H_{66}Mg_2O_{12}P_4Se_8$ requires C, 33.21; H, 4.18 %.

IR (Nujol, NaCl): *v*(H_2O) 3321 br, 1608 m, *v*(P-C) 1430 s, 1036 m, 880 m, 692 m cm^{-1}; **^{1}H NMR** (400 MHz, $[D_6]$DMSO, 25 °C) $\delta = 8.1$ (4H, m, ArH), 7.4 (4H, m, ArH), 3.6 (10H, m, $O\mathit{CH_2}CH_2$), 3.3 (s, H_2O), 1.8 (10H, m, $OCH_2\mathit{CH_2}$); **^{13}C NMR** (100 MHz, $[D_6]$DMSO, 25 °C) $\delta = 130.9$, 130.8, 129.8, 126.8, 126.7, 67.0, 25.2; **^{31}P NMR** (162 MHz, $[D_6]$DMSO, 25 °C, 65 % H_3PO_4) $\delta = 32.9$ (s + 2 d satellites, $^1J_{P\text{-}Se} = -396$ Hz, -698 Hz); **^{77}Se NMR** (76 MHz, $[D_6]$DMSO, 25 °C, Me_2Se) $\delta = 40.5$ (d, $^1J_{P\text{-}Se} = -698$ Hz).

2: Synthesis of **1** performed at room temperature. 0.25 g, yield 60 %. mp 125-128 °C (decomposition); Found: C, 35.94; H, 4.41. $C_{24}H_{36}MgO_6P_2Se_4$ requires C, 35.04; H, 4.41 %.

IR (KBr): *v*(H_2O) 3306 br , 2970 m, 1610 s, *v*(P-C) 1436 s, 1036 s, 888 br s, 690 s cm^{-1}. **^{1}H NMR** (400 MHz, $[D_6]$DMSO, 25 °C) $\delta = 8.1\text{-}6.9$ (10H, 6 x m, ArH), 3.6 (10H, m, $O\mathit{CH_2}CH_2$), 3.3 (s, H_2O), 1.7 (10H, m, $OCH_2\mathit{CH_2}$); **^{13}C NMR** (100 MHz, $[D_6]$DMSO, 25 °C) $\delta = 126.2 - 130.9$ (8C, ar. C), 67.0, 25.2; **^{31}P NMR** (162 MHz, $[D_6]$DMSO, 25 °C, 65 % H_3PO_4) $\delta = 32.9$ (s + two d satellites, $^1J_{P\text{-}Se} = -395$ Hz, -697 Hz), 43.6 (m, slow decomposition in $[D_6]$DMSO into a yet unknown compound); **^{31}P NMR** (162 MHz, $[D_8]$THF, 25 °C, 65 % H_3PO_4) $\delta = 37.3$ (s + two d satellites, $^1J_{P\text{-}Se} = -392$ Hz, -704 Hz); **^{77}Se NMR** (76 MHz, $[D_6]$DMSO, 25 °C, Me_2Se) $\delta = 40.5$ (d, $^1J_{P\text{-}Se} = 698$ Hz), 131.0 (d, $^1J_{P\text{-}Se} = -710$ Hz).

3: A mixture of 266 mg (0.5 mmol) Woollins' reagent and 123 mg (0.5 mmol) $[Mn(OAc)_2(H_2O)_4]$ was dissolved in 8 mL THF. The yellow cloudy solution was stirred overnight at room temperature, and filtered. The filtrate was layered with 60 mL hexane. Storage of the solution at room temperature for 2 weeks produced yellow crystals. 0.28 g, yield 60 %. mp 105 °C (decomposition); Found: C, 33.25; H, 4.18. $C_{24}H_{36}MnO_6P_2Se_4$ requires C, 33.78; H, 4.25 %.

IR (KBr): *v*(H_2O) 3306 br, 2973 m, 1601 m, *v*(P-C) 1435 s, 1027 s, 870 br s, 687 s cm^{-1}.

X-ray Crystallographic Study

Data for **1** and **2** were collected on a Stoe Ipds II diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data) using the Shelxtl program package [21]. Hydrogen atoms were placed in calculated positions, non-hydrogen atoms were assigned anisotropic thermal parameters. Disordered components were refined with isotropic thermal parameters. A summary of crystal data and refinement parameters is given in table 1.

CCDC nos. 624864-624866 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1 Details of the X-ray data collection and refinements.

Compound	**1**	**2**	**3**
Formula	$C_{52}H_{82}Mg_2O_{14}P_4Se_8$	$C_{24}H_{36}MgO_6P_2Se_4$	$C_{24}H_{36}MnO_6P_2Se_4$
Formula weight	1735.36	822.62	853.25
T/K	170(2)	150(2)	105(2)
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*P*ca2$_1$	*P*2$_1$/c	*P*2$_1$/c
a/Å	42.900(9)	15.527(3)	9.6810(19)
b/Å	15.650(3)	41.777(8)	15.539(3)
c/Å	10.115(2)	9.782(2)	42.003(8)
β/°	90	91.38(3)	95.33(3)
V/Å^3	6791(2)	6343(2)	6291(2)
Z	4	8	8
μ/mm^{-1}	4.474	4.782	5.185
F(000)	3448	3248	3352
Reflections collected	45508	19615	38688
Unique data	15777	10383	12175
R_{int}	0.0843	0.0684	0.0968
Parameters	739	651	673
*w*R$_2$ (all data)	0.1928	0.2967	0.1901
R_1 [I>2σ(I)]	0.0661	0.0997	0.0660

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