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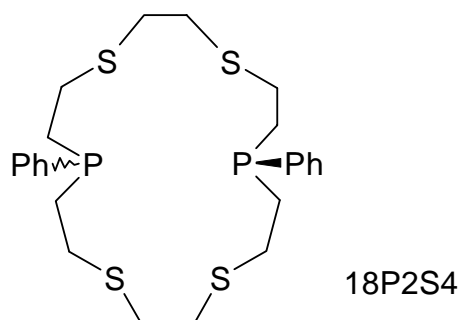
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Contents Page

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Preparation, characterisation and crystal structures of complexes of 1,10-diphenyl-1,10-diphospha-4,7,13,16-tetrathiacyclooctadecane (18P2S4) containing nickel, iron and ruthenium are described.



Synthesis and Coordination Chemistry of a Diphospha-tetrathia Macrocycle, 1,10-diphenyl-1,10-diphospha-4,7,13,16-tetrathiacyclooctadecane.

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Summary

Reaction of 1,2-dichloroethane with $\text{PhP}(\text{CH}_2\text{CH}_2\text{SH})_2$ and caesium carbonate affords 1,10-diphenyl-1,10-diphospha-4,7,13,16-tetrathiacyclooctadecane (18P2S4) in high yield (*ca.* 90%). 18P2S4 slowly decomposes in solution to afford insoluble $\text{PhP}(\text{S})(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2)_2\text{P}(\text{S})\text{Ph}$ which was characterised by single crystal X-ray diffraction. Reaction of 18P2S4 with $[\text{Ni}(\text{H}_2\text{O})_6](\text{BF}_4)_2$ or $\text{Fe}(\text{BF}_4)_2$ affords $[\text{M}(18\text{P}2\text{S}4)](\text{BF}_4)_2$ (M = Ni or Fe). The structure of $[\text{Ni}(18\text{P}2\text{S}4)]^{2+}$ is a tetragonally distorted octahedron in which there are two short Ni-S bonds [2.2152(6)Å] and two long Ni-S bonds [2.9268(6)Å]. For comparison the structure of $[\text{Ni}(9\text{PS}2)]^{2+}$ was determined and found to have a similar, but less marked distortion, in which the difference between the long and short bonds is *ca.* 0.5 Å. In contrast the structure of $[\text{Fe}(18\text{P}2\text{S}4)]^{2+}$ is octahedral with approximately equal Fe-S bonds. The electrospray mass spectra of the cations $[\text{M}(9\text{PS}2)]^{2+}$ and $[\text{M}(18\text{P}2\text{S}4)]^{2+}$ (M= Ni or Fe) all display ethene loss from the ligands as has been previously observed with trithiacyclononane complexes. The results of P-C and C-S bond rupture were also observed in the reaction of ruthenium(III) triflate with 9PS2 which unexpectedly afforded crystals containing $[\text{Ru}_2(\text{S})_2(18\text{P}2\text{S}4)_2]$, in which the two ruthenium centres are bridged by two sulfides and the two 18P2S4 ligands coordinated only through the phosphine centres. Also present in the crystals was one equivalent of tetrathiacycloundecane (12S4).

Introduction

In recent years there has been considerable interest in macrocyclic systems containing soft donors. We have studied this class of compound as potential ligands for use in radiopharmacy since they bind strongly to soft metals such as Cu(I), Re(II), Hg(II) which have useful radioisotopes.¹ Macrocyclic thioethers have been the focus of much attention,² but the stronger binding properties of phosphines has encouraged the study of all phosphine containing systems³ as well as a variety of mixed phosphine-thioether systems.⁴ We have previously investigated the synthesis and coordination chemistry of 1-phenyl-1-phospha-4,7-dithiacyclononane (9PS2).⁵⁻⁸ In this paper we report a new synthesis and coordination chemistry of 1,10-diphenyl-1,10-diphospha-4,7,13,16-tetrathiacyclooctadecane (18P2S4).

Experimental Section

All reactions were carried out under an atmosphere of dinitrogen using standard Schlenk tube and vacuum line techniques, and all solvents were freshly distilled under a dinitrogen atmosphere and over an appropriate drying agent. The compounds $\text{PhP}(\text{CH}_2\text{CH}_2\text{SH})_2$,⁹ 9PS2⁷ and $[\text{Fe}(\text{9PS2})_2][\text{BF}_4]_2$ ⁷ were prepared by literature methods. Electrospray mass spectra were recorded on a Finnigan MAT LCQ ion trap mass spectrometer (University of Kent Department of Biosciences, Wellcome Trust Protein Science Facility). Samples were prepared by dissolution of ~1mg of sample in 1ml acetonitrile, this solution was further diluted by a factor of 10 and 20 μl injected directly into the ionisation chamber. A range of cone voltages were applied from 15 – 60 V. Ion detection was in positive mode only. IR spectra were recorded as KBr pellets using a Biorad FTS175C FTIR spectrometer and UV-visible spectra were recorded using a Unicam UV 500 spectrophotometer.

Synthesis of 1,10-diphenyl-1,10-diphospha-4,7,13,16-tetrathia-cyclooctadecane

$\text{PhP}(\text{CH}_2\text{CH}_2\text{SH})_2$ (4 ml, 5.105 g, 0.022 moles) was dissolved in anhydrous DMF (150 ml) with caesium carbonate (7.164 g, 0.022 moles). The resulting suspension was heated to 70 °C with stirring. Dichloroethane (1.7 ml, 0.022 moles) was mixed with DMF (100 ml) and this solution was added dropwise to the reaction mixture via a peristaltic pump, over 10 –12 hours. The DMF was removed *in vacuo* and the residue extracted with dichloromethane (100 ml), washed with 1M sodium hydroxide (2 x 50 ml) and water (2 x 50 ml). The resulting solution was dried over NaSO_3 and filtered. The dichloromethane was removed *in vacuo* leaving a sticky white/cream residue of 18P2S4. Purification by redissolving in a small volume of dichloromethane and filtering through silica followed by evaporation *in vacuo*

afforded an oil. Yield 5.523g, 90%. Microanalysis: Found C 55.4, H 6.7; $C_{24}H_{34}P_2S_4$ requires C 56.2, H 6.7%; ^{31}P NMR (CD_2Cl_2) -24.7. 1H NMR (CD_2Cl_2) 7.7-7.1 (m, 10 H, Ph), 2.9-1.9 (m, 24H, CH_2). IR spectrum (KBr disk) 2914 s, 1673 m, 1433 s, 1264 m, 1191 m, 741 s, 484 $w\text{ cm}^{-1}$. Upon standing in CH_2Cl_2 insoluble crystals of 18P2S4S2 are formed. IR spectrum (KBr disk) 2920 s, 1653 w, 1436 s, 1287 m, 1188 s, 1120 m, 995 w, 899 w, 804 m, 746 s, 700 m, 593 m, 524 $m\text{ cm}^{-1}$.

Preparation of $[Ni(9PS2)_2][BF_4]_2$

A solution of $Ni(BF_4)_2 \cdot 6H_2O$ (0.184g, 0.6 mmol) in acetonitrile (5cm^3) was added to a vigorously stirred solution of 9PS2 (0.358g, 1.4 mmol) in acetonitrile (4 cm^3) under a dinitrogen atmosphere. The solution turned dark green in colour instantly and was left stirring for 15 minutes. An olive green precipitate was formed upon addition of dry diethyl ether (10 cm^3). The precipitate was filtered and washed with diethyl ether ($2 \times 10\text{ cm}^3$). Yield: 0.3g (29%). Microanalysis: Found C 38.4, H 4.6; $C_{24}H_{34}B_2F_8NiP_2S_4$ requires C 38.7, H 4.6%; UV-VIS (MeCN) λ_{max} nm, ($\epsilon/M^{-1}\text{ cm}^{-1}$) 316(17653), 674(94).

Preparation of $[Ni(18P2S4)][BF_4]_2$

A solution of $Ni(BF_4)_2 \cdot 6H_2O$ (0.42 g, 1.23 mmol) in acetonitrile (20 cm^3) was added dropwise to a stirred solution of 18P2S4 (0.93 g, 1.82 mmol) in dichloromethane (20 cm^3). Stirring was continued for 1 hour and then the crude product was precipitated by addition of diethylether which was then recrystallised as a green powder from acetonitrile. Yield: 0.64 g (70 %). Microanalysis Found C 39.0, H 4.8, $C_{24}H_{34}B_2F_8NiP_2S_4$ requires C 38.7, H 4.6%. UV-VIS (MeCN) λ_{max} nm, ($\epsilon/M^{-1}\text{ cm}^{-1}$) 318 (16555) 615 (104).

Preparation of $[Fe(18P2S4)][BF_4]_2$

A solution of $Fe(BF_4)_2 \cdot 6H_2O$ (0.53 g, 1.57 mmol) in acetonitrile (20 cm^3) was added dropwise to a stirred solution of 18P2S4 (0.98 g, 1.92 mmol) in dichloromethane (20 cm^3). Stirring was continued for 1 hour and then the crude product was precipitated by addition of diethylether which was then recrystallised as a red powder from acetonitrile. Yield: 0.93 g (80 %). Microanalysis Found C 39.1, H 4.7, $C_{24}H_{34}B_2F_8FeP_2S_4$ requires C 38.8, H 4.6%.

Preparation of $[Ru_2(S)_2(18P2S4)_2]$

Ruthenium trichloride (0.20 g, 0.97 mmol) was refluxed in MeOH (10 cm^3) with silver triflate (0.74 g, 2.9 mmol) for 1 h to give a dark brown solution. The filtered solution was added to 9PS2 (0.51 g, 2.0 mmol) dissolved in MeCN (10 cm^3) and the mixture was refluxed 18 h. Upon cooling pale yellow crystals of $[Ru_2(S)_2(18P2S4)_2] \cdot 12S_4$ formed.

Crystal Structure Determination of $[Ni(18P2S4)][BF_4]_2$

A single crystal of the complex grown by slow evaporation of MeCN was mounted on a glass fibre using Apiezon vacuum grease. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$).¹⁰ Intensities were integrated¹¹ from several series of exposures, each exposure covering 0.3° in ω , and the total data set being a hemisphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.¹² The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections.¹³ All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. The structure of the dicationic metal complex has crystallographically imposed inversion symmetry. Thus the asymmetric unit contains half a molecule of the Ni cation, a single BF₄ anion. One of the CH₂CH₂ residues is disordered over two sites (65:35) and this was well modelled. Complex neutral-atom scattering factors were used.¹⁴

Crystal Structure Determinations of 18P2S4S2, [Ni(9PS2)₂](BF₄)₂, [Fe(18P2S4)](BF₄)₂ and [Ru₂(S)₂(18P2S4)₂].12S4

The data was collected using the microcrystal diffraction facility on station 9.8 of the Synchrotron Radiation Source, CLRC Daresbury Laboratory.^{15,16} The data was collected on a Bruker AXS SMART CCD area-detector diffractometer. The crystals, which had been grown by slow evaporation of MeCN, were mounted on the end of a two-stage glass fibre with perfluoropolyether oil, and cooled by a nitrogen-gas stream.¹⁷ The wavelength was calibrated by measurement of the unit cell parameters of a standard crystal of known structure. Data collection nominally covered a sphere of reciprocal space by three series of ω -rotation exposure frames with different crystal orientation ϕ angles. Reflection intensities were integrated using standard procedures,¹⁸ allowing for the plane-polarised nature of the primary synchrotron beam. Corrections were applied semiempirically for absorption and incident beam decay.¹⁹ Unit cell parameters were refined from the observed ω angles of all strong reflections in the complete data sets.²⁰ The structure was solved by routine automatic direct methods and refined by least-squares refinement of all unique measured F^2 values.²¹

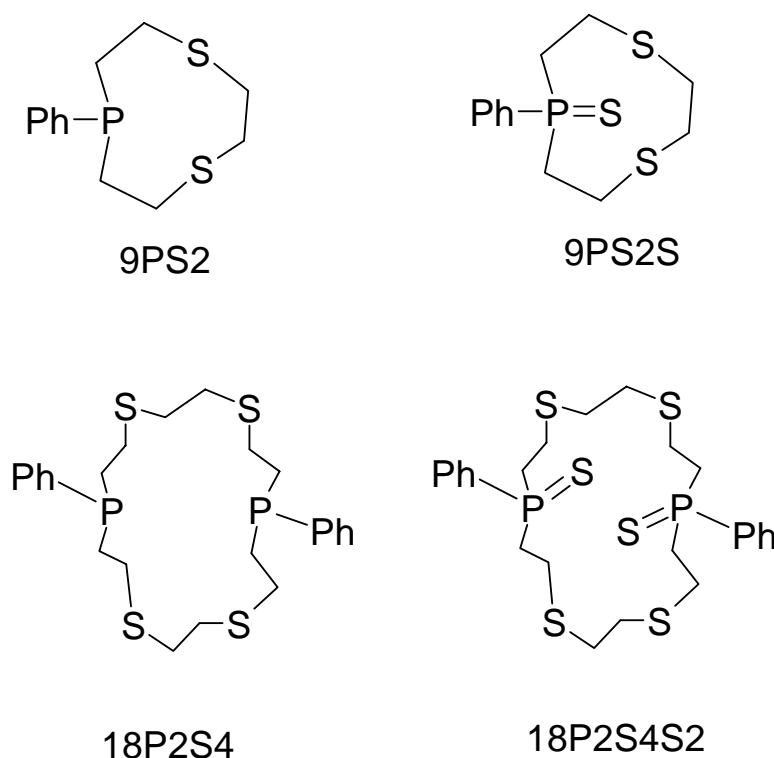
Table 1. Details of X-ray Analyses of 18P2S4S2, [Ni(18P2S4)](BF₄)₂, [Ni(9PS2)₂](BF₄)₂, [Fe(18P2S4)](BF₄)₂ and [Ru₂(S)₂(18P2S4)₂].14S4

	18P2S4S2	[Ni(18P2S4)](BF ₄) ₂	[Ni(9PS2) ₂](BF ₄) ₂	[Fe(18P2S4)](BF ₄) ₂	[Ru ₂ (S) ₂ (18P2S4) ₂].12S4
formula	C ₂₄ H ₃₄ P ₂ S ₆	C ₂₄ H ₃₄ B ₂ F ₈ NiP ₂ S ₄	C ₂₄ H ₃₄ B ₂ F ₈ NiP ₂ S ₄	C ₂₄ H ₃₄ B ₂ F ₈ FeP ₂ S ₄	C ₅₆ H ₈₄ P ₄ Ru ₂ S ₁₄
fw	576.81	745.02	745.02	742.16	1532.09
λ (Å)	0.6872	0.71073	0.6948	0.6900	0.6948
space group	P2 ₁ /n	P2 ₁ /n	P $\bar{1}$	P $\bar{1}$	P2 ₁ /n
temp (K)	150(2)	173(2)	150(2)	150(2)	150(2)
cell constants					
a (Å)	10.7703(15)	10.3392(14)	9.8902(5)	10.0486(3)	15.0803(7)
b (Å)	10.5334(14)	13.703(2)	10.2918(5)	11.5779(3)	12.6682(6)
c (Å)	12.0899(16)	11.3041(13)	15.2327(7)	14.0704(4)	18.8409(8)
α (deg)			91.971(2)	75.330(2)	
β (deg)	93.343(3)	111.288(10)	93.796(2)	88.262(2)	111.229(2)
γ (deg)			107.470(2)	65.870(2)	
V (Å ³)	1369.2(3)	1492.3(4)	1473.34(12)	1440.26(7)	3355.1(3)
Z	2	2	2	2	2
D _c (g cm ⁻³)	1.399	1.658	1.679	1.711	1.517
μ (mm ⁻¹)	0.629	1.104	1.119	0.994	1.017
Reflections measured	13395	9375	13596	14818	7948
Independent reflections	3877	3402	7382	7794	5290
R _{int}	0.0292	0.0208	0.0188	0.0272	0.0421
R ₁ (all data)	0.0802	0.0449	0.0445	0.0370	0.0528
wR ₂ (all data)	0.2164	0.0842	0.0930	0.0888	0.1271

Results and Discussion

Ligand Synthesis

The reported high dilution synthesis of 9PS2 (scheme 1) via the reaction of $\text{PhP}(\text{CH}_2\text{CH}_2\text{SH})_2$ with 1,2-dichloroethane and Cs_2CO_3 often produces a mixture of products that are difficult to separate even by HPLC.⁷ The mixture is most easily characterised by ^{31}P NMR spectroscopy. The desired product, 9PS2, has a resonance at -16.0 ppm, but sometimes a peak is observed at +47.5 ppm characteristic of $\text{PhPS}(\text{CH}_2\text{CH}_2\text{S})_2\text{CH}_2\text{CH}_2$ (9PS2S)⁵ and also a peak at -24.7 ppm attributable to the 2+2 product 18P2S4, which has been previously prepared in 10% yield by the reaction of dilithiophenylphosphide with the mustard 1,2-bis-(2-chloroethylthio)ethane.²² Only one ^{31}P NMR resonance was reported²² for 18P2S4 at -24.6 ppm, which is presumably due to one of the two possible isomers, resulting from *cis* or *trans* disposition of the phenyl groups, or alternatively both isomers fortuitously have the same ^{31}P NMR chemical shift. We occasionally observe further weak peaks in the region -24 to -26 ppm which could be assigned to the second isomer or higher oligomers.



Scheme 1

Typically isomers in this class of compound can be separated and have similar, but distinct chemical shifts. For example, $\text{PhP}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2)_2\text{SO}$ has two isomers with ^{31}P NMR shifts of -25.4 and -27.3 ppm.^{4a} Also *cis*- $\text{PhP}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2)_2\text{PPh}$ (-25.0, -

27.51 ppm) and *trans*-PhP(CH₂CH₂SCH₂CH₂CH₂)₂PPh (-24.43, -26.66 ppm) have been characterised.^{4b} All five of the possible isomers of 4,7,13,16-tetraphenyl-1,10-dithia-4,7,13,16-tetraphosphacyclooctadecane have been isolated,^{4c} while only one isomer of 8,12-diphenyl-1,5-dithia-8,12-diphosphacyclotetradecane (Ph₂[14]aneP₂S₂) has been isolated.^{4d}

Once the presence of 18P₂S₄ in the reaction mixture had been established the method was modified to optimise its yield to ca. 90% by slow addition of 1,2-dichloroethane to a mixture of PhP(CH₂CH₂SH)₂ and caesium carbonate.

Leaving dichloromethane solutions of 18P₂S₄ in air for several days results in formation of crystals of PhP(S)(CH₂CH₂SCH₂CH₂SCH₂CH₂)₂P(S)Ph (18P₂S₄S₂) which were found to be insoluble in CH₂Cl₂, DMSO, THF, acetone, toluene and MeCN. The presence of the sulfide is indicated by the appearance of a P=S bond stretch in the infra-red spectrum at 593cm⁻¹. Similar acyclic compounds have absorptions in range 610-600 cm⁻¹.²³ The synthesis of 9PS₂S has been previously reported by treatment of Mo(CO)₃(9PS₂) with sulfur,⁵ but it is also observed to form if 9PS₂ is left to stand in solution. As insolubility precluded characterisation by solution spectroscopic techniques the structure of 18P₂S₄S₂ was established by a single crystal X-ray diffraction study. The molecular structure is shown in Figure 1 and selected bond lengths and angles are given in Table 2. The isomer present in the crystal has a *trans* disposition of the phenyl groups and has crystallographically imposed inversion symmetry. The S-C-C-E units adopt typical *anti* conformations and the thioether groups are hence exodentate in contrast to the *gauche* conformation in the smaller 9PS₂S.⁵ The phosphorus-sulfur double bond length [1.8979(15)Å] is significantly shorter than in 9PS₂S [1.963(3)Å], and is short compared with other terminal phosphine-sulfide bond lengths in the Cambridge Crystallographic Database (average 1.965 Å range 1.905-2.072 Å).²⁴

Table 2. Selected Bond lengths (Å) and angles (°) for 18P2S4S2.

S(2)–C(5)	1.811(3)	S(2)–C(4)	1.814(3)
S(1)–C(2)	1.814(3)	S(1)–C(3)	1.814(3)
P(1)–C(1)	1.816(3)	P(1)–C(6)	1.819(3)
P(1)–C(7)	1.808(3)	P(1)–S(3)	1.8979(15)
C(1)–C(2)	1.531(4)	C(5)–C(6)	1.532(4)
C(4)–C(3)	1.527(4)		
C(5)–S(2)–C(4)	101.67(14)	C(2)–S(1)–C(3)	102.35(14)
C(1)–P(1)–C(6)	106.20(13)	C(1)–P(1)–C(7)	105.88(13)
C(1)–P(1)–S(3)	114.28(11)	C(6)–P(1)–C(7)	105.20(14)
C(6)–P(1)–S(3)	111.81(11)	C(7)–P(1)–S(3)	112.79(11)

^a Estimated standard deviations are given in parentheses.

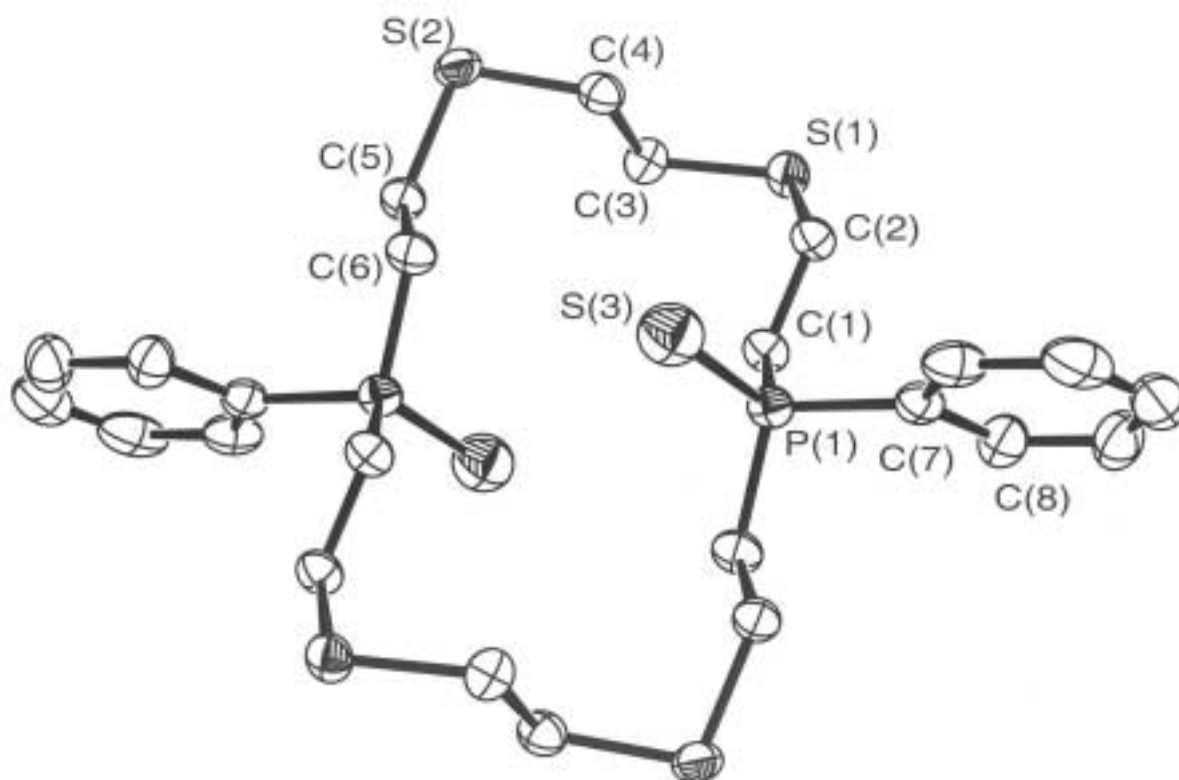


Fig 1 Molecular structure of 18P2S4S2 showing the atom labelling system. Atoms are represented as 50% probability ellipsoids.

Coordination Chemistry

No coordination chemistry of 18P2S4 has been previously reported and we wished to compare its performance as a ligand with 9PS2 as well as the related thiamacrocycles 9S3 and

18S6. Reaction of 18P2S4 with $[\text{Ni}(\text{H}_2\text{O})_6](\text{BF}_4)_2$ affords $[\text{Ni}(18\text{P}2\text{S}4)](\text{BF}_4)_2$ in ca. 70% yield. $[\text{Ni}(18\text{P}2\text{S}4)](\text{BF}_4)_2$ crystallises in the monoclinic space group $\text{P}2_1/\text{n}$. The structure of the centrosymmetric pseudo octahedral cation is shown in Figure 2 and selected bond lengths and angles are given in Table 3. The Ni-P(1) distance is 2.2004(6)Å. The Ni-S(1) distance [2.2152(6)Å] is considerably shorter than Ni-S(2) [2.9268(6)Å]. The Ni-S bond lengths in $[\text{Ni}(18\text{S}6)](\text{pic})_2$ are more even, 2.389(1), 2.397(1), 2.377(1)Å.²⁵ The short Ni-S(1) bond length is typical of four coordinated square planar nickel thioether complexes.²⁶ The overall geometry is similar to $[\text{M}(18\text{S}6)](\text{BPh}_4)_2$ (M= Pd or Pt) which have weak axial interactions of 3.2330(17) and 3.380(3)Å.²⁷ Presumably the stronger field 18P2S4 ligand ($\Delta_o = 16260$ versus 12290 cm^{-1}) is increasing the preference for nickel to be square planar. The geometry appears to be metal driven as the ligand can form more symmetric octahedral complexes (*vide infra*). We have noted previously that C-S bonds can be lengthened in 9S3 complexes due to π -acceptance into the C-S σ^* orbitals.²⁸ The C-S bond lengthening is greater if the C-S bond lies in the plane of the metal t_{2g} orbitals as would be expected on the basis that overlap between metal t_{2g} and C-S σ^* orbitals is better if the C-S bonds and the t_{2g} orbitals are coplanar. The same effect is observed in $[\text{Ni}(18\text{P}2\text{S}4)]^{2+}$ with in-plane S(1)-C(2) 1.839(2) Å being longer than out-of-plane S(1)-C(3) 1.818(3) Å, although the effect is not observed in $[\text{Ni}(18\text{S}6)]^{2+}$.²⁵ The bond lengthening caused by coordination can be gauged by comparison with the C-S bonds in 9S3 [1.820(5) and 1.823(5)Å]²⁹ and in 9PS2S [range 1.792(9) to 1.815(9)Å (average 1.804Å)].⁵ These bonds are significantly longer than in the larger fourteen-membered *trans*-1,8-diphenyl-1,8-diphospha-4,12-dithia-cyclotetradecane (*trans*-14P2S2) [1.733(7) and 1.759(8) Å] possibly reflecting the strain in the smaller nine-membered rings.^{4b}

Table 3. Selected Bond Lengths (Å) and Bond Angles (°)^a for $[\text{Ni}(18\text{P}2\text{S}4)](\text{BF}_4)_2$

Ni - P(1)	2.2004(6)	Ni - S(1)	2.2152(6)
Ni - S(2)	2.9268(6)	P(1) - C(6a)	1.790(4)
P(1) - C(6b)	1.943(7)	P(1) - C(11)	1.808(2)
P(1) - C(1)	1.822(2)	S(1) - C(3)	1.818(3)
S(1) - C(2)	1.839(2)	S(2) - C(4)	1.798(2)
S(2) - C(5a)	1.848(4)	S(2) - C(5b)	1.808(7)
C(1) - C(2)	1.531(3)	C(3) - C(4)	1.520(3)
C(5a) - C(6a)	1.513(9)	C(5B) - C(6b)	1.529(14)
P(1) - Ni - P(1)'	180.0	P(1) - Ni - S(1)	86.47(2)
P(1) - Ni - S(1)'	93.53(2)	S(1) - Ni - S(1)'	180.0
P(1) - Ni - S(2)	98.47(2)	P(1) - Ni - S(2)'	81.53(2)
S(1) - Ni - S(2)	82.52(2)	S(1) - Ni - S(2)'	97.48(2)

S(2) - Ni - S(2)'	180.0	C(6a) - P(1) - C(11)	115.3(3)
C(6b) - P(1) - C(11)	95.4(4)	C(6a) - P(1) - C(1)	98.1(2)
C(6b) - P(1) - C(1)	115.0(3)	C(6a) - P(1) - Ni	108.81(16)
C(6b) - P(1) - Ni	114.5(2)	C(11) - P(1) - C(1)	107.31(10)
C(11) - P(1) - Ni	118.95(7)	C(1) - P(1) - Ni	105.70(8)
C(3) - S(1) - C(2)	100.47(13)	C(3) - S(1) - Ni	108.48(8)
C(2) - S(1) - Ni	108.10(8)	C(4) - S(2) - C(5a)	94.0(3)
C(4) - S(2) - C(5b)	117.0(4)		

^a Estimated standard deviations are given in parentheses.

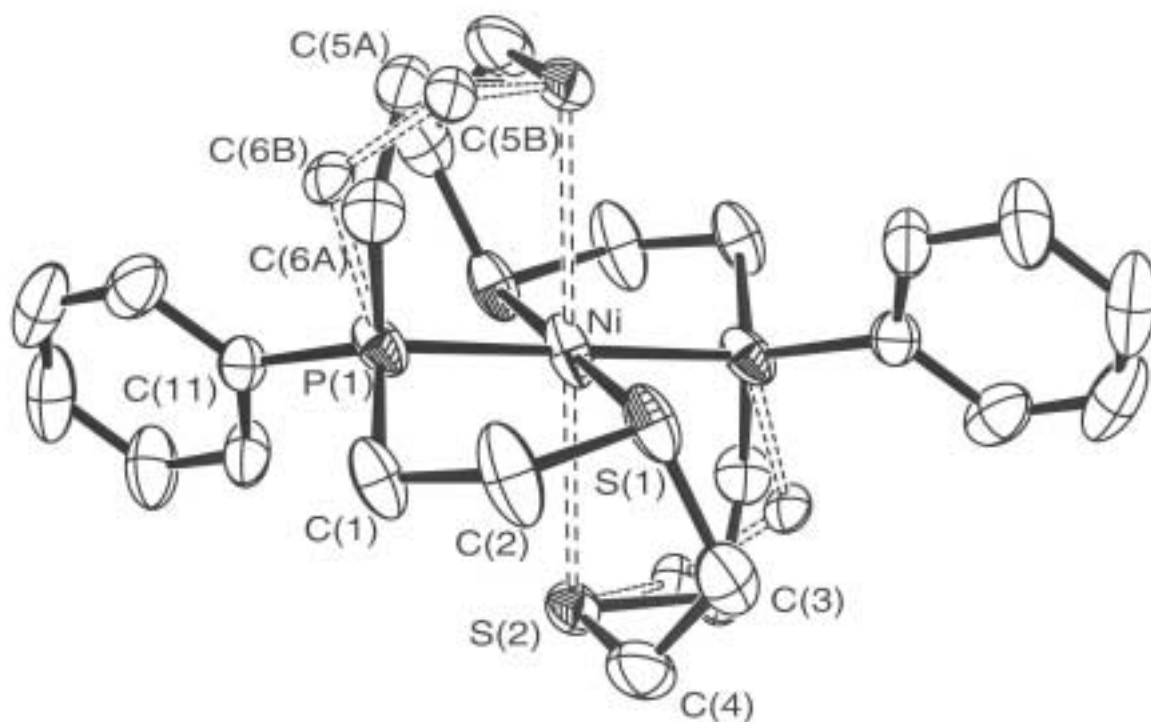


Fig 2 Molecular structure of $[\text{Ni}(\text{18P2S4})]^{2+}$ showing the atom labelling system. Atoms are represented as 50% probability ellipsoids. Broken lines indicate the disordered part of the molecule.

For comparison the crystal structure of $[\text{Ni}(\text{9PS2})_2](\text{BF}_4)_2$ was determined.⁷ The compound crystallises in the $P\bar{1}$ space group with two molecules in the unit cell. Both molecules have crystallographically imposed centres of symmetry. The two molecules have some crystallographically significant differences, but similar geometries and further discussion will be limited to molecule 1 shown in Figure 3 (selected bond lengths and angles for both molecules are presented in Table 4). The nickel atom has tetragonally distorted octahedral geometry but the distortion is less marked than in $[\text{Ni}(\text{18P2S4})]^{2+}$, possibly due to the more rigid nature of the nine-membered ring. The two short bonds $[\text{Ni}(1)\text{-S}(5)$ 2.2263(5) and $\text{Ni}(1)\text{-}$

P(2) 2.2095(5) Å] are approximately 0.5 Å shorter than those in the elongated S-Ni-S axis [Ni(1)-S(8) 2.7812(6) Å]. Previous EXAFS studies of this complex were unable to resolve the two lengths.⁷ Crystal structures of [Ni(9S3)₂]²⁺ again reveal a higher degree of octahedral symmetry [Ni(9S3)₂](BF₄)₂ [Ni-S 2.377(1)- 2.400(1) Å³⁰] and [Ni(9S3)₂](Br)₂.4(H₂O) [Ni-S 2.3749(16) - 2.4077(15) Å³¹] while palladium and platinum analogues are pseudo square planar.³²⁻³⁴

Table 4. Selected Bond Lengths (Å) and Bond Angles (°)^a for [Ni(9PS2)₂][BF₄]₂

Molecule 1		Molecule 2	
Ni(1) - P(2)	2.2095(5)	Ni(17) - P(18)	2.1930(5)
Ni(1) - S(5)	2.2263(5)	Ni(17) - S(21)	2.2115(4)
Ni(1) - S(8)	2.7812(6)	Ni(17) - S(24)	2.7919(5)
P(2) - C(11)	1.8086(19)	P(18) - C(27)	1.8018(19)
P(2) - C(3)	1.8208(19)	P(18) - C(26)	1.819(2)
P(2) - C(10)	1.8295(19)	P(18) - C(19)	1.833(2)
C(3) - C(4)	1.519(3)	C(19) - C(20)	1.522(3)
C(4) - S(5)	1.834(2)	C(20) - S(21)	1.821(2)
S(5) - C(6)	1.8094(19)	S(21) - C(22)	1.832(2)
C(6) - C(7)	1.521(3)	C(22) - C(23)	1.513(7)
C(7) - S(8)	1.813(2)	C(23) - S(24)	1.807(2)
S(8) - C(9)	1.816(2)	S(24) - C(25)	1.827(2)
C(9) - C(10)	1.523(3)	C(25) - C(26)	1.532(3)
Molecule 1		Molecule 2	
P(2) - Ni(1) - P(2)'	180.0	P(18) - Ni(17) - P(18)'	180.0
P(2) - Ni(1) - S(5)'	92.515(17)	P(18) - Ni(17) - S(21)'	91.618(17)
P(2) - Ni(1) - S(5)	87.485(17)	P(18) - Ni(17) - S(21)	88.382(17)
S(5) - Ni(1) - S(5)'	180.0	S(21) - Ni(17) - S(21)'	180.0
P(2) - Ni(1) - S(8)'	94.557(16)	P(18) - Ni(17) - S(24)'	97.657(16)
P(2) - Ni(1) - S(8)	85.443(16)	P(18) - Ni(17) - S(24)	82.343(16)
S(5) - Ni(1) - S(8)'	94.536(16)	S(21) - Ni(17) - S(24)'	94.148(16)
S(5) - Ni(1) - S(8)	85.464(16)	S(21) - Ni(17) - S(24)	85.852(16)
C(11) - P(2) - C(3)	104.76(9)	C(27) - P(18) - C(26)	106.00(18)
C(11) - P(2) - C(10)	106.97(9)	C(27) - P(18) - C(19)	107.86(9)
C(3) - P(2) - C(10)	106.58(9)	C(26) - P(18) - C(19)	107.43(10)
C(11) - P(2) - Ni(1)	121.53(6)	C(27) - P(18) - Ni(17)	116.10(6)
C(3) - P(2) - Ni(1)	105.55(6)	C(26) - P(18) - Ni(17)	110.63(7)
C(10) - P(2) - Ni(1)	110.43(7)	C(19) - P(18) - Ni(17)	108.50(6)
C(6) - S(5) - C(4)	100.05(9)	C(20) - S(21) - C(22)	100.48(10)
C(6) - S(5) - Ni(1)	106.84(7)	C(20) - S(21) - Ni(17)	102.09(6)
C(4) - S(5) - Ni(1)	107.91(6)	C(22) - S(21) - Ni(17)	109.42(7)
C(9) - S(8) - C(7)	103.05(10)	C(23) - S(24) - C(25)	101.96(10)

^a Estimated standard deviations are given in parentheses.

The phenyl group is approximately coplanar with the nine-membered ring as has been observed in $[\text{Mo}(\text{CO})_2\text{Br}_2(9\text{PS}2)]$,⁵ $[\text{Cu}(\eta^1\text{-}9\text{PS}2)(\eta^3\text{-}9\text{PS}2)]^+$,⁷ and $[\text{Hg}(9\text{PS}2)_2]^{2+}$.⁷ A contrasting perpendicular orientation of the phenyl ring has been observed in $[\text{Mo}(\text{CO})_3(9\text{PS}2)]$.⁵

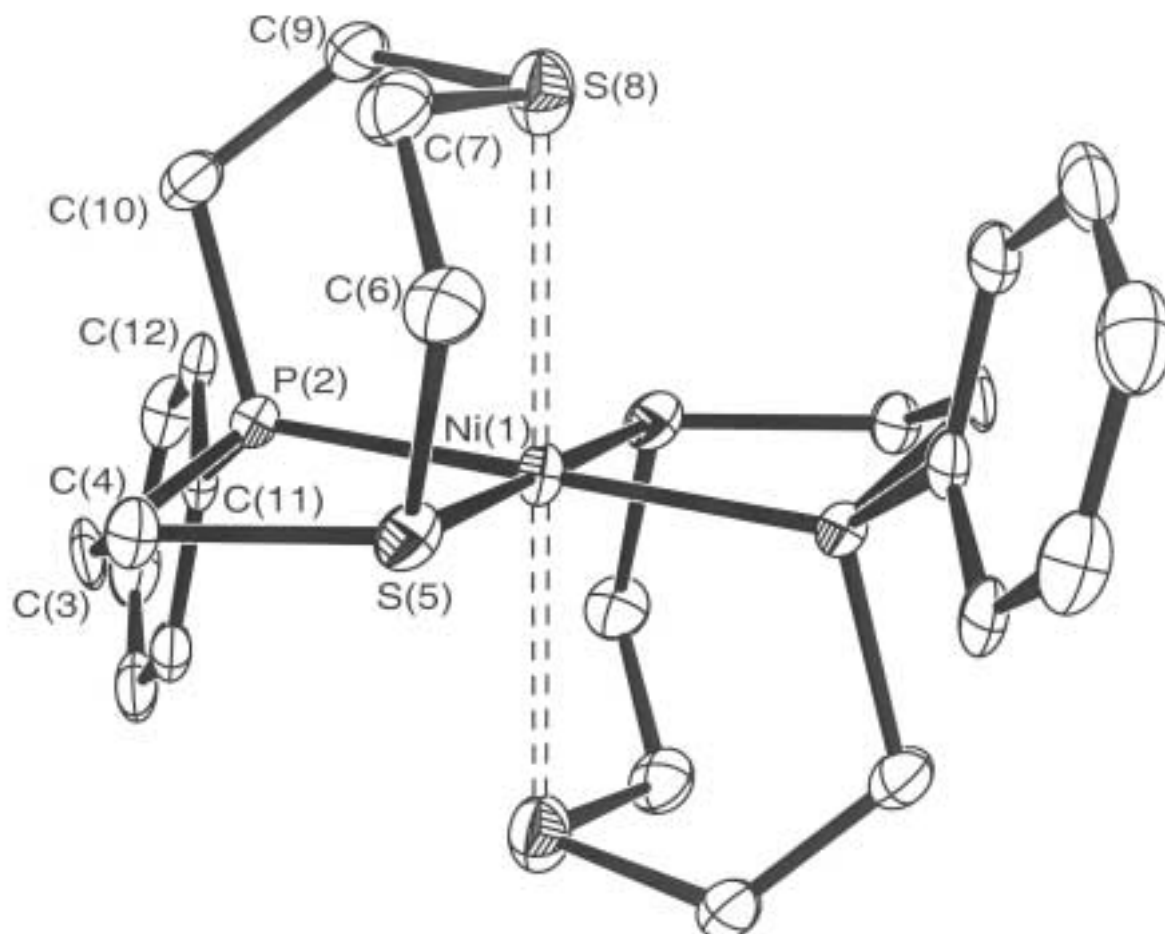


Fig 3 Molecular structure of $[\text{Ni}(9\text{PS}2)_2]^{2+}$ showing the atom labelling system. Atoms are represented as 50% probability ellipsoids.

The expected correlation is observed for in plane and out of plane C-S bonds [in plane S(5)-C(4) 1.834(5), out of plane S(5)-C(6) 1.8094(19) Å]. Not surprisingly there is no significant variation for the more remote thioether. A much smaller increase is observed for the in plane P(2)-C(10) 1.8295(19) compared with the out of plane P(2)-C(3) 1.8208(19) Å. Comparisons for these P-C bond lengths with those expected in an uncoordinated nine-membered ring are difficult to establish. To date crystalline 9PS2 has not been obtained. 9PS2S containing a

pentavalent phosphorus has P-C bond lengths of 1.831(7) and 1.828(9) Å.³ The less strained *trans*-14P2S2 has comparatively long P-C bonds 1.854(7) and 1.837(7) Å.^{4b} In the eleven-membered rings 2,6,10-triphenyl-2,6,10-triphosphabicyclo(9.4.0)pentadeca-11(1),12,14-triene and 6-phenyl-6-phospha-2,10-dithiabicyclo(9.4.0)pentadeca-11(1),12,14-triene³⁵ the P-C bonds lengths are in range 1.834(8) - 1.862(8) and in the twelve-membered 1,5,9-triphospha-1,5,9-tris(2-propyl)cyclododecane the range is 1.831(5) to 1.862(5) Å.³⁶ As has been observed previously the P-C bonds do not appear to be significantly lengthened by coordination.⁸

The electrospray mass spectra of [Ni(9PS2)₂](BF₄)₂ and [Ni(18P2S4)](BF₄)₂ are similar at cone voltages of 15 and 45V. The major peaks in the 15V spectra are presented in Table 5. The base peaks are those for [Ni(9PS2)₂]²⁺ and [Ni(18P2S4)]²⁺ and as has been observed previously in this class of compound peaks are observed due to ethene loss.⁸

Table 5. 15V Electrospray Mass spectrometry Data for [M(9PS2)₂](BF₄)₂ and [M(18P2S4)](BF₄)₂ (M = Fe and Ni)

Species	Metal	M/z	Relative Intensity
[M(9PS2) ₂ (BF ₄) ⁺	Fe	654.9	7
	Ni	656.7	10
[M(18P2S4)(BF ₄) ⁺	Fe	654.9	5
	Ni	656.7	4
[M(9PS2) ₂ F] ⁺	Ni	589.0	17
[M(18P2S4)F] ⁺	Fe	587.0	28
	Ni	589.0	14
[M(9PS2) ₂ - H] ⁺	Fe	566.9	26
[M(18PS2) ₂] ²⁺	Fe	284.0	100
	Ni	285.1	100
[M(18P2S4)] ²⁺	Fe	284.1	100
	Ni	285.0	100
[M(9PS2) ₂ - C ₂ H ₄] ²⁺	Fe	270.0	33
	Ni	271.0	4
[M(18P2S4) - C ₂ H ₄] ²⁺	Fe	270.0	12
	Ni	271.0	19
[M(9PS2) ₂ - 2(C ₂ H ₄)] ²⁺	Fe	256.0	13
	Ni	257.1	2
[M(18P2S4) - 2(C ₂ H ₄)] ²⁺	Fe	256.0	9
	Ni	257.1	9
[M(9PS2) ₂ - 3(C ₂ H ₄)] ²⁺	Fe	242.0	7
	Ni	242.3	33
[M(18P2S4) - 3(C ₂ H ₄)] ²⁺	Fe	242.0	*
	Ni	242.3	29
[M(18P2S4) - 4(C ₂ H ₄)] ²⁺	Fe	228.0	6

* Peak obscured.

Reaction of 18P2S4 with Fe(BF₄)₂ affords [Fe(18P2S4)](BF₄)₂, the structure of which was determined by single crystal X-ray crystallography. The compound crystallises in the P $\bar{1}$ space group with two molecules in the unit cell. The structure of molecule 1 is shown in Figure 4 and selected bond and angles for both molecules are given in Table 6. Both cations are pseudo octahedral and have crystallographically imposed centres of symmetry. Although both cations adopt similar geometries there are significant differences, perhaps the most noticeable being the Fe-P bond distances, 2.2477(4) Å in molecule 1 and 2.2296(4) Å in molecule 2. The longer Fe-P bond length in molecule 1 is accompanied by shorter Fe-S distances. The Fe-P distance in the previously determined structure of [Fe(9PS2)₂][BF₄]₂ is [2.2244(7)Å].⁸ The Fe-S bond lengths [Molecule 1 2.2412(4) and 2.2439(4) Å, Molecule 2 2.2565(4) and 2.2503(4) Å] are similar to those found in [Fe(9PS2)₂][BF₄]₂ [2.2445(7) and 2.2516(7)Å]. The variation of C-S bond lengths is less marked than that observed in [Fe(9PS2)₂][BF₄]₂, however electrospray mass spectroscopy (Table 5) shows that both complexes lose ethene in a similar manner.⁸

Table 6. Selected Bond lengths (Å) and angles (°)^a for [Fe(18P2S4)](BF₄)₂.

Molecule 1		Molecule 2	
Fe(1)–P(1)	2.2477(4)	Fe(1')–P(1')	2.2296(4)
Fe(1)–S(1)	2.2412(4)	Fe(1')–S(1')	2.2565(4)
Fe(1)–S(2)	2.2439(4)	Fe(1')–S(2')	2.2503(4)
P(1)–C(1)	1.8348(16)	P(1')–C(1')	1.8349(17)
P(1)–C(6)	1.8389(16)	P(1')–C(6')	1.8391(16)
P(1)–C(11)	1.8173(16)	P(1')–C(11')	1.8161(16)
S(1)–C(2)	1.8392(16)	S(1')–C(2')	1.8319(17)
S(1)–C(3)	1.8178(19)	S(1')–C(3')	1.8242(17)
S(2)–C(4)	1.826(2)	S(2')–C(4')	1.8178(17)
S(2)–C(5)	1.8281(17)	S(2')–C(5')	1.8358(16)
C(1)–C(2)	1.525(2)	C(1')–C(2')	1.523(2)
C(3)–C(4)	1.506(3)	C(3')–C(4')	1.512(2)
C(5)–C(6)	1.515(2)	C(5')–C(6')	1.523(2)
P(1)–Fe(1)–P(1A)	180.0	P(1')–Fe(1')–P(1'B)	180.0
P(1)–Fe(1)–S(1)	87.761(14)	P(1')–Fe(1')–S(1')	87.835(14)
P(1A)–Fe(1)–S(1)	92.239(14)	P(1'B)–Fe(1')–S(1')	92.165(14)
P(1)–Fe(1)–S(2)	92.386(14)	P(1')–Fe(1')–S(2')	92.099(14)
P(1A)–Fe(1)–S(2)	87.614(14)	P(1')–Fe(1')–S(2'B)	87.901(14)
S(1)–Fe(1)–S(1A)	180.0	S(1')–Fe(1')–S(1'B)	180.0
S(1)–Fe(1)–S(2)	90.042(16)	S(1')–Fe(1')–S(2')	90.494(14)
S(1)–Fe(1)–S(2A)	89.958(16)	S(1')–Fe(1')–S(2'B)	89.506(14)
S(2)–Fe(1)–S(2A)	180.0	S(2')–Fe(1')–S(2'B)	180.0
Fe(1)–P(1)–C(1)	106.62(5)	Fe(1')–P(1')–C(1')	108.94(6)
Fe(1)–P(1)–C(6A)	108.83(5)	Fe(1')–P(1')–C(6'B)	108.45(5)

Fe(1)–P(1)–C(11)	125.47(5)	Fe(1')–P(1')–C(11')	122.39(5)
C(1)–P(1)–C(6A)	105.50(8)	C(1')–P(1')–C(6'B)	104.27(8)
C(1)–P(1)–C(11)	103.45(7)	C(1')–P(1')–C(11')	105.74(7)
Fe(1)–S(1)–C(2)	107.98(5)	Fe(1')–S(1')–C(2')	106.51(6)
Fe(1)–S(1)–C(3)	104.20(6)	Fe(1')–S(1')–C(3')	104.85(6)
C(2)–S(1)–C(3)	101.88(8)	C(2')–S(1')–C(3')	102.10(8)
Fe(1)–S(2)–C(4)	105.48(7)	Fe(1')–S(2')–C(4')	104.66(5)
Fe(1)–S(2)–C(5)	106.38(6)	Fe(1')–S(2')–C(5')	107.59(5)
C(4)–S(2)–C(5)	102.38(8)	C(4')–S(2')–C(5')	101.74(8)

^a Estimated standard deviations are given in parentheses.

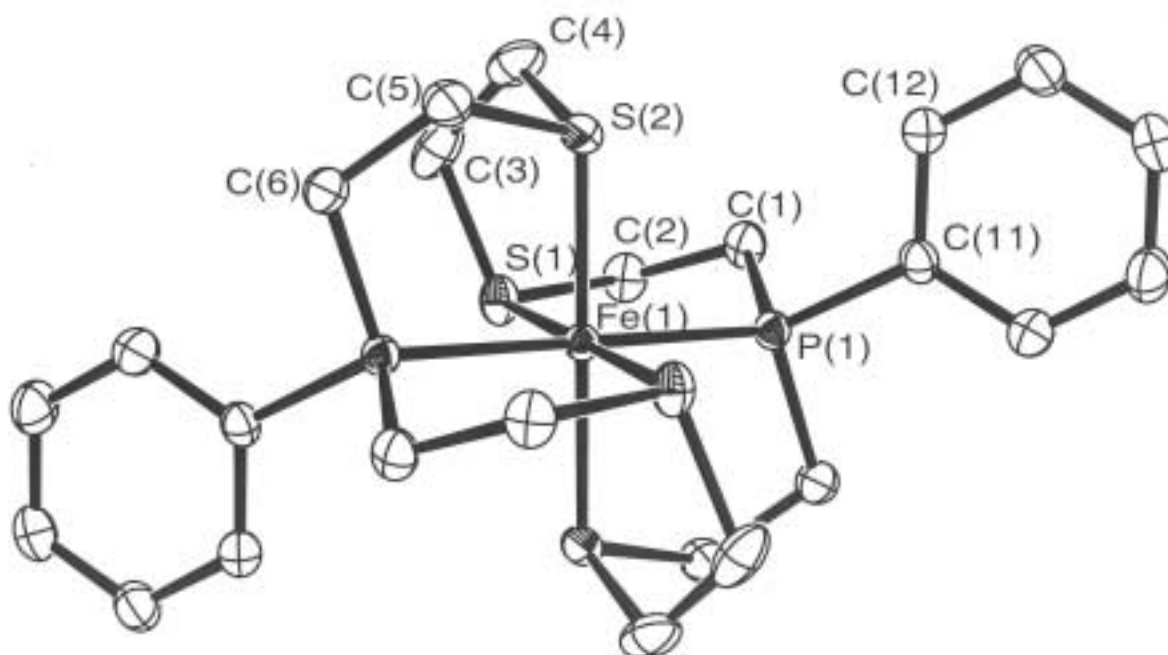


Fig 4 Molecular structure of $[\text{Fe}(18\text{P}2\text{S}4)]^{2+}$ showing the atom labelling system. Atoms are represented as 50% probability ellipsoids.

A final 18P2S4 compound was prepared unexpectedly by the reaction of ruthenium triflate with 9PS2 in MeCN. The bulk of the material obtained from the reaction was $[\text{Ru}(\text{MeCN})_6](\text{CF}_3\text{SO}_3)_2$, but two other products were identified from a crystal obtained from the reaction mixture. The X-ray crystal structure revealed the presence of $[\text{Ru}_2(\text{S})_2(18\text{P}2\text{S}4)_2]$ (Figure 5) and tetrathiacycloundecane (Figure 6) in the unit cell. Both compounds result from either extensive rearrangement of 9PS2, indicating C-S and P-C rupture and formation, or from trace impurities in the 9PS2. The $[\text{Ru}_2(\text{S})_2(18\text{P}2\text{S}4)_2]$ molecule has a crystallographic inversion centre and contains two ruthenium centres bridged by two sulfides and two 18P2S4

ligands coordinated through the phosphine centres [Ru-P 2.4245(13) and 2.4256(14) Å]. The ruthenium centres have no metal-metal bond [Ru-Ru 3.839 Å] and can be considered to have very distorted tetrahedral geometries [S-Ru-S 89.45(3), P-Ru-P 139.30(4)°]. The 18P2S4 ligands have their phenyl groups in a *cis* configuration and the S-C-C-X linkages are *anti*. As expected the S-C bond distances are relatively uniform and short in the range 1.818-1.808 Å since there is no thioether coordination. The diruthenium disulfide core appears not to have been previously characterised by X-ray crystallography.

Table 7. Selected Bond Lengths (Å) and Bond Angles (°)^a for [Ru₂(S)₂(18P2S4)₂]

Ru(1) - P(3)	2.4245(13)	Ru(1) - P(18)	2.4256(14)
Ru(1) - S(2')	2.6256(12)	Ru(1) - S(2)	2.7751(9)
P(3) - C(12)	1.809(5)	P(3) - C(8)	1.829(5)
P(3) - C(4)	1.831(4)	P(18) - C(27)	1.831(5)
P(18) - C(23)	1.838(4)	P(18) - C(19)	1.842(5)
C(4) - C(5)	1.527(7)	C(5) - S(6)	1.817(4)
S(6) - C(7)	1.818(5)	C(7) - C(22)	1.548(9)
C(8) - C(9)	1.528(5)	C(9) - S(10)	1.810(5)
S(10) - C(11)	1.811(5)	C(11) - C(26)	1.512(7)
C(19) - C(20)	1.520(6)	C(20) - S(21)	1.808(4)
S(21) - C(22)	1.799(5)	C(22) - C(7)	1.548(9)
C(23) - C(24)	1.523(6)	C(24) - S(25)	1.809(4)
S(25) - C(26)	1.818(5)	C(26) - C(11)	1.512(7)
P(3) - Ru(1) - P(18)	139.30(4)	P(3) - Ru(1) - S(2')	108.97(4)
P(18) - Ru(1) - S(2)'	106.20(4)	P(3) - Ru(1) - S(2)	102.47(3)
P(18) - Ru(1) - S(2)	97.67(4)	S(2)' - Ru(1) - S(2')	89.45(3)
Ru(1)' - S(2) - Ru(1)	90.55(3)		

^a Estimated standard deviations are given in parentheses.

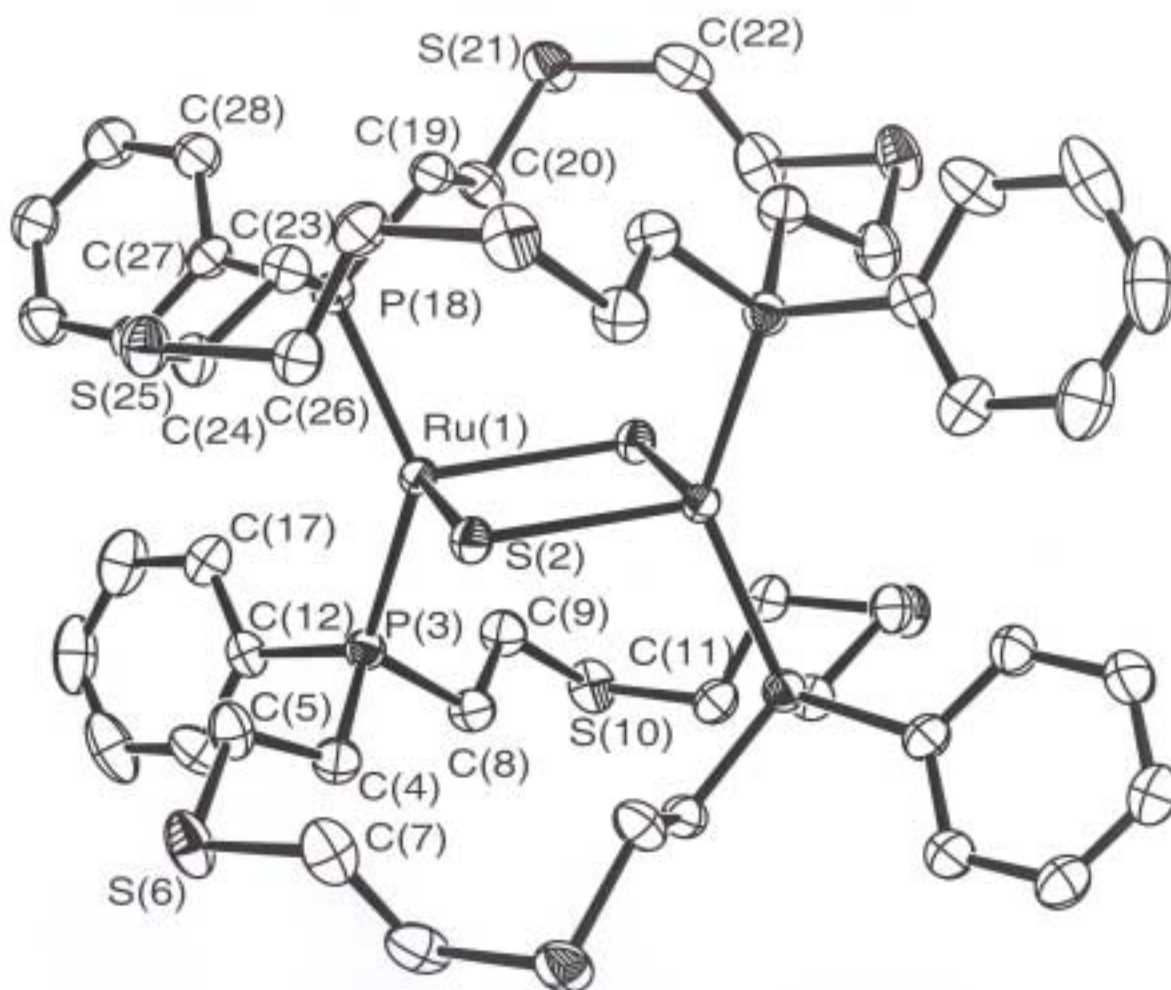


Fig 5 Molecular structure of $[\text{Ru}_2(\text{S})_2(18\text{P}2\text{S}4)]$ showing the atom labelling system. Atoms are represented as 50% probability ellipsoids.

The second compound present in the unit cell is surprisingly tetrathiacycloundecane ($12\text{S}4$). The molecule is disordered but has essentially the same geometry as a previous reported structure.³⁷

Table 8. Selected Bond Lengths (Å) and Bond Angles (°)^a for $12\text{S}4$

S(51) - C(56B')	1.795(15)	S(51) - C(52A)	1.797(19)
S(51) - C(56A')	1.808(10)	S(51) - C(52B)	1.819(18)
C(52A) - C(53A)	1.56(3)	C(53A) - S(54)	1.773(17)

C(52B) - C(53B)	1.47(3)	C(53B) - S(54)	1.87(2)
S(54) - C(55A)	1.814(10)	S(54) - C(55B)	1.823(15)
C(55A) - C(56A)	1.513(18)	C(55B) - C(56B)	1.530(14)
<hr/>			
C(52A) - S(51) - C(52A')	90.3(5)	C(56B) - S(51) - C(56B')	98.8(6)
C(53A) - S(54) - C(55A)	102.7(5)	C(55B) - S(54) - C(53B)	101.4(6)

^a Estimated standard deviations are given in parentheses.

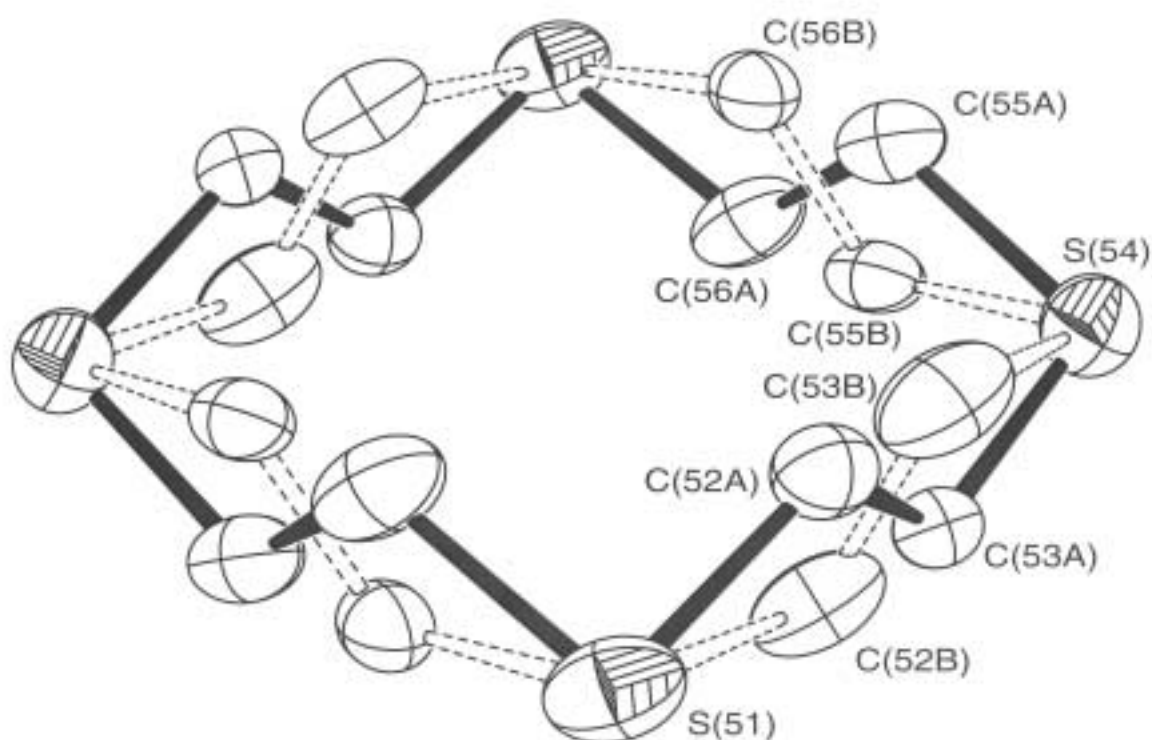


Fig 6 Molecular structure of 12S4 showing the atom labelling system. Atoms are represented as 50% probability ellipsoids. Broken lines indicate the disordered part of the molecule.

It is difficult to fully rationalise the formation of these two products although C-S and P-C bond rupture are well established in the coordination chemistry of 9S3 and 9PS2.⁸ Previously reported trends suggest that 9PS2 would be more prone to C-S or P-C rupture when coordinated to ruthenium rather than iron.²⁸ It is perhaps worth mentioning that in preliminary experiments using 1-cyclohexyl-1-phospha-4,7-dithiacyclononane reaction with $\text{Fe}(\text{BF}_4)_2$

afforded $[\text{Fe}(\text{9S3})_2][\text{BF}_4]_2$ in which again P-C bond rupture and C-S bond formation had occurred.

Conclusions

18P2S4 can be prepared conveniently in high yield without the use of mustard compounds and is a stronger field ligand than 18S6 due to the presence of the phosphine groups. 18P2S4 and 9PS2 display similar coordination chemistries with greater flexibility of geometry observed for the larger ring. The crystal structures of $[\text{Ni}(\text{9PS2})_2]^{2+}$ and $[\text{Fe}(\text{18P2S4})]^{2+}$ both contain two independent cations with significant different M-S and M-P bond lengths indicating that the M-C and M-S bonds are soft and easily distorted. Lengthening of C-P and C-S bonds is observed upon coordination of 18P2S4 due to the population of C-P and C-S σ^* orbitals which results in the observation of ethene loss by electrospray mass spectrometry. This lability of the C-P and C-S bonds is also observed in the formation of $[\text{Ru}_2(\text{S})_2(\text{18P2S4})_2]$ and 18S4 and unfortunately limits the applicability of 9PS2 and 18P2S4 for the development of new radiopharmaceuticals which require chemically stable complexes.

Acknowledgments. We thank the EPSRC for funding. We acknowledge the provision of time on DARTS, the UK national synchrotron radiation service at the CLRC Daresbury Laboratory, through funding by the EPSRC.

Supporting Information Available: X-ray crystallographic files, in CIF format for 18P2S4S2, $[\text{Ni}(\text{18P2S4})](\text{BF}_4)_2$, $[\text{Ni}(\text{9PS2})_2](\text{BF}_4)_2$, $[\text{Fe}(\text{18P2S4})](\text{BF}_4)_2$ and $[\text{Ru}_2(\text{S})_2(\text{18P2S4})_2] \cdot 12\text{S4}$

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