

www.elsevier.nl/locate/ica

Inorganica Chimica Acta 294 (1999) 170-178

Inorganica Chimica Acta

Synthesis and coordination chemistry of 1-phenyl-1-phospha-4,7-dithiacyclononane

Philip J. Blower^a, Alan V. Chadwick^b, John C. Jeffery^c, Gregory E.D. Mullen^b, Anne K. Powell^d, Spencer N. Salek^a, Raymond J. Smith^a, Michael J. Went^{b,*}

^a Department of Biosciences, University of Kent, Canterbury, Kent, CT2 7NJ, UK

^b School of Physical Sciences, University of Kent, Canterbury, Kent, CT2 7NR, UK

^c Department of Inorganic Chemistry, The University, Bristol, BS8 1TS, UK

^d School of Chemical Sciences, University of East Anglia, Norwich, NR4 7JT, UK

Received 24 December 1998; accepted 2 March 1999

Abstract

Reaction of PhP(CH₂CH₂SH)₂ with 1,2-dichloroethane and Cs₂CO₃ under high dilution conditions affords 1-phenyl-1-phospha-4,7-dithiacyclononane (L) as an oil in 52% yield. The geometry of L has been probed by ¹H NMR spectroscopy, which indicates an equilibrium mixture containing *gauche* S–C–C–S and S–C–C–P segments, and molecular mechanics calculations which find a lowest energy endodentate conformation minimum and also energetically accessible exodentate minima. Endo- and exodentate conformations are observed in the crystal structure of $[Cu(\eta^1-L)(\eta^3-L)][PF_6]$ (1) formed by the reaction of L with $[Cu(NCMe)_4][PF_6]$. Reaction of Hg(ClO₄)₂ with L affords $[HgL_2][ClO_4]_2$ (2) whose structure has also been established by X-ray diffraction. The mercury ion is in a very distorted octahedral environment with two short Hg–P bonds (average 2.404 Å) and four long Hg–S bonds (average 3.092 Å). Reaction of L with AgBF₄ or Ni(BF₄)₂ or CoBr₂ or Fe(BF₄)₂ affords $[AgL_2][BF_4]$ (3), $[NiL_2][BF_4]_2$ (4), $[CoL_2]Br_2$ (5) and $[FeL_2][BF_4]_2$ (6), respectively, which were characterised by FAB mass spectroscopy and elemental analysis. Cyclic voltammetry studies were used to compare the redox properties of 4, 5 and 6 with their trithiacyclononane (9S3) analogues and in compound 4 the ligand L was found to stabilise Ni in the oxidation states 0, I, II and III. UV–Vis spectroscopic measurements show that L is a stronger field ligand than 9S3. EXAFS studies were also performed on 4, 5 and 6, which established that all three complexes are six-coordinate. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Copper complexes; Nickel complexes; Phosphathiamacrocycle complexes; Thioether complexes

1. Introduction

Our study of mixed phosphathiamacrocycles combines the areas of phosphine coordination chemistry and the more recent developments in thiamacrocycle coordination chemistry [1,2]. The chemistry of complexes containing phosphine ligands has been studied intensively and a vast number of uni- and bidentate phosphine complexes are known, some of which have important catalytic properties. In comparison to phosphines, thioethers are relatively weakly bound ligands [3]. However, thioether macrocycles and in particular 1,4,7-trithiacyclononane (9S3) are capable of producing metal complexes of high thermodynamic and kinetic stability [4,5]. The unique properties of 9S3 are a result of the combination of the 'macrocyclic effect' with a conformation which is ideal for facial tridentate coordination, and consequently many 9S3 complexes exhibit interesting electronic and electrochemical properties [5]. These observations led to the speculation as to whether the combination of the nine-membered ring conformational properties with phosphine donor centres might offer complexes with extreme chemical robustness and electronic versatility. Recent reports suggest that syntheses of triphosphacyclononane complexes using a Group 6 metal tricarbonyl template are difficult [6]. Our studies have so far concentrated on the synthesis of mixed phosphathiacyclononanes [1,2].

^{*} Corresponding author. Tel.: + 44-1227-823 540; fax: + 44-1227-827 558.

E-mail address: m.j.went@ukc.ac.uk (M.J. Went)

We have previously reported the synthesis of 1phenyl-phospha-4,7-dithiacyclononane (L) via a tricarbonylmolybdenum template cyclisation followed by treatment with sulfur and then reduction with sodium naphthalenide [2]. In this paper we give full details of a high dilution synthesis of L and its coordination chemistry with Cu⁺, Hg²⁺, Ag⁺, Co²⁺, Ni²⁺ and Fe²⁺ ions [1]. The aim of this work was to determine to what extent the conformational preferences of L mimic those of 9S3, and hence to confirm or refute the suggestion that nine-membered phosphine containing macrocycles might form exceptionally robust complexes of soft metals.

2. Experimental

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 compound PhP(CH₂CH₂SH)₂ was prepared by a literature method [7]. Fast atom bombardment spectra were recorded by the EPSRC mass spectrometry service at the University of Swansea with a VG ZAB-E instrument from NOBA matrices. Electronic spectra were recorded in quartz cells on a Philips PU8730 UV-Vis scanning spectrophotometer. ¹H NMR spectra were recorded by the EPSRC NMR service with a Varian INOVA 600 MHz spectrometer. ³¹P NMR spectra were recorded with a JEOL GX 270 instrument referenced to 85% H₃PO₄ (external). Simulation and iterative fitting of the ¹H NMR spectra was performed using LAOCOON PC [8]. Molecular-mechanics calculations were carried out using HYPER-CHEM (Release 3) [9]. Structures were minimised with conjugate gradients (Polak-Ribiere algorithm) using the MM + force field until the gradients were less than 0.01 kcal mol⁻¹ Å⁻¹. Cyclic voltammetric measurements were performed on an EG&G Model 362 scan-

Table 1 Analytical ^a and physical data

ning potentiostat using Condecon 310 as the data analysis software. All measurements were carried out using a glassy carbon electrode (BAS Technicol, Stockport, UK) as the working electrode, platinum gauze as the auxiliary electrode and Ag | AgCl as the reference electrode. Elemental analyses were performed by A.J. Fassam at the University of Kent. Analytical and physical data for the new compounds are given in Table 1.

2.1. Preparation of $PhP(CH_2CH_2S)_2CH_2CH_2$ (L)

A solution of PhP(CH₂CH₂SH)₂ (2.0 g, 8.7 mmol) and 1,2-dichloroethane (0.860 g, 8.7 mmol) in DMF (50 cm³) was added dropwise to a stirred suspension of Cs₂CO₃ (3.114 g, 9.55 mmol) in DMF (100 cm³) at 60°C over 24 h. The solvent was then removed in vacuo and the residue extracted with dichloromethane (3×50) cm³). The combined extracts were filtered and washed with 1 M NaOH (2×50 cm³) and water (2×50 cm³). The solvent was removed in vacuo and the residue flash chromatographed on a silica column (4×32 cm) eluting with $CHCl_3$ - CH_2Cl_2 (3:2) to afford L (1.16 g, 52%). ¹H NMR (CDCl₃): δ 7.55–7.29 (m, 5H, Ph), 3.181 [dddd, 2H, H¹, J(H¹H²) 14.52(2), J(H¹H³) 3.37(2), J(H¹H⁴) 7.21(2), J(PH) 22.13], 3.058 [m, 2H, H⁵H^{5'}, J 8.10(1), J' 2.83(1), J_{gem} – 15.29(1), J(PH) 0.61], 3.041 $[dddd, 2H, H^2, J(H^1H^2) 14.52(2), J(H^2H^3) 10.08(2),$ J(H²H⁴) 3.49(2), J(PH) 10.38], 2.849 [m, 2H, H⁶H^{6'}, J 8.10(1), J' 2.83(1), J_{gem} – 15.29(1)], 2.682 [dddd, 2H, H³, $J(H^1H^3)$ 3.37(2), $J(H^2H^3)$ 10.08(2), $J(H^3H^4)$ 14.90(2), J(PH) 3.13], 2.321 [dddd, 2H, H⁴, J(H¹H⁴) 7.21(2), $J(H^2H^4)$ 3.49(2), $J(H^3H^4)$ 14.90(2), J(PH) 3.59]. ${}^{31}P{}^{1}H{}$ (CDCl₃) - 16.9 ppm.

2.2. Preparation of $[CuL_2][PF_6]$ (1)

 $[Cu(NCMe)_4][PF_6]$ (0.082 g, 0.22 mmol) was added to a solution of L (0.12 g, 0.468 mmol) in MeCN (4 cm³). After stirring for 5 min Et₂O (20 cm³) was added and the mixture left overnight at 4°C to produce off-white

Compound	Appearance	Yield (%)	Analysis (%)	m/z		
			C	Н	Ν	
L	colourless oil	52	56.5 (56.2)	6.9 (6.7)	_	^b 256 (M ⁺)
$[CuL_2][PF_6]$ (1)·MeCN	white solid	80	40.7 (41.0)	4.6 (4.9)	1.8 (1.8)	-
$[HgL_2][ClO_4]$ (2)	white solid	61	31.5 (31.6)	3.3 (3.7)	-	_
$[AgL_2][BF_4]$ (3)	white solid	72	40.4 (40.8)	4.5 (4.8)	_	$^{\circ}$ 621 (M ⁺ – BF ₄)
$[NiL_2][BF_4]_2$ (4)	green solid	73	39.0 (38.7)	4.6 (5.2)	_	$^{\circ}657 (M^{+} - BF_{4})$
$[CoL_2]Br_2$ (5)	green solid	73	38.9 (39.4)	6.7 (4.7)	_	$^{\circ}652 (M^{+}-Br)$
$[FeL_2][BF_4]_2$ (6)	red solid	88	38.4 (38.9)	4.8 (4.6)	_	$^{\circ}655 (M^{+} - BF_{4})$

^a Calculated values are given in parentheses.

^b Electron impact (EI) mass spectrometry.

^c Fast atom bombardment (FAB) mass spectrometry.

crystals which were isolated by filtration and dried under vacuum to afford $[CuL_2][PF_6]$ (0.134 g, 80%).

2.3. Preparation of $[HgL_2][ClO_4]_2$ (2)

Addition of $Hg(ClO_4)_2$ (0.08 g, 0.19 mmol) to L (0.10 g, 0.39 mmol) in nitromethane (25 cm³) resulted in precipitation of $[HgL_2][ClO_4]_2$ (0.11 g, 61%).

2.4. Preparation of $[AgL_2][BF_4]$ (3)

A solution of AgBF₄ (0.114 g, 0.585 mmol) in MeOH (10 cm³) was added to L (0.300 g, 1.170 mmol) in MeOH (4 cm³). After 5 h the solid white product was collected by filtration and washed with Et₂O (4 × 20 cm³) to afford [AgL₂][BF₄] (0.296 g, 72%).

2.5. Preparation of $[NiL_2][BF_4]_2$ (4)

A solution of Ni(BF₄)₂ (0.136 g, 0.585 mmol) in CH₃NO₂ (15 cm³) was added to L (0.300 g, 1.170 mmol) in CH₃NO₂ (15 cm³) and stirred for 2 h. The solution was then cooled in the fridge and the dark green product collected by filtration and washed with Et₂O (4 × 20 cm³) to afford [NiL₂][BF₄]₂ (0.318 g, 73%).

2.6. Preparation of $[CoL_2]Br_2$ (5)

To a solution of L (0.100 g, 0.39 mmol) in CH₃NO₂ (25 cm³) was added CoBr₂ (0.043 g, 0.195 mmol). After stirring for 30 min the supernatant was removed by filtration and the solid dried under vacuum to afford $[CoL_2]Br_2$ (0.104 g, 73%) as a green powder.

2.7. Preparation of $[FeL_2][BF_4]_2$ (6)

To a solution of L (0.100 g, 0.39 mmol) in CH₃CN (4 cm³) was added Fe(BF₄)₂ (0.046 g, 0.2 mmol) in CH₃CN (5 cm³). The solution turned red immediately and after stirring for 15 min diethyl ether (10 cm³) was added to form a bright red precipitate which was isolated by filtration and washed with diethyl ether (2 × 10 cm³) to afford [FeL₂][BF₄]₂ (0.130 g, 88%).

2.7.1. Crystal structure determination of 1

Details of the X-ray structure analyses are summarised in Table 2. A crystal of $[CuL_2][PF_6]$ (1) (0.30 × 0.35 × 0.58) was obtained from acetonitrile solution. Intensity data were collected on a Siemens R3m/V diffractometer with graphite monochromated Mo K α X-radiation ($\lambda = 0.710$ 73 Å). Cell constants were obtained from least-squares refinement of the setting angles of 25 centred reflections in the range 22° < θ < 25°. The data were collected in the ω scan mode and two standard reflections were measured every 50 reflections. The data were corrected for Lorentz and polarisation Table 2

Details of the X-ray structure analyses for compounds $[Cu(\eta^1-L)-(\eta^3-L)][PF_6] \cdot (MeCN)$ (1) and $[HgL_2][CIO_4]_2 \cdot 1/2(MeCN)$ (2)

	1	2
Formula	C ₂₆ H ₃₇ CuF ₆ NP ₃ S ₄	C ₂₅ H _{35.5} Cl ₂ HgN _{0.5} O ₈ P ₂ S ₄
$M_{ m f}$	762.3	932.71
Space group	$P\overline{1}$	$P2_1/n$
Temp. (K)	294	138
Cell constants		
a (Å)	9.631(3)	10.233(1)
b (Å)	12.446(2)	28.756(2)
c (Å)	14.404(5)	22.655(2)
α (°)	101.12(2)	
β (°)	94.22(3)	97.67(1)
γ (°)	96.26(2)	
V (Å ³)	1676.2(8)	6607(1)
Ζ	2	8
$D_{\rm c} ({\rm g} {\rm cm}^{-3})$	1.51	1.88
$\mu ({\rm mm}^{-1})$	1.084	5.22
$2\theta_{\rm max}$	50.0	50.8
T_{\min}, T_{\max}	0.33, 0.43	0.23, 0.44
No. of reflections	4127, 3	10271, 2
$I > n\sigma(I), n$		
$wR_2 = (F^2, \text{ all reflections})$		0.0840
$wR(F, F_{o} > 6\sigma(F_{o}))$	0.105	
$R_1(F, F_0 > 4\sigma(F_0))$		0.0351
$R (F, F_{o} > 6\sigma(F_{o}))$	0.075	

^a $wR_2 = [\Sigma[w(F_o^2 - F_o^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$ and $w^{-1} = [\sigma^2(F_o^2) + (0.0157P)^2 + 32.844P]$ and $P = [\max(F_o, 0) + 2F_o^2]/3$.

factors and a semi-empirical absorption correction was applied. The structure was solved by Patterson synthesis using Siemens SHELXTL PLUS (VMS) [10] to locate all the non-hydrogen atoms. Hydrogen atoms were added in calculated riding positions with fixed isotropic U. Refinement was by full-matrix least-squares.

2.7.2. Crystal structure determination of 2

Crystals of $[HgL_2][ClO_4]_2$ (2) were obtained from MeCN solution as poorly formed white plates. A crystal $(0.41 \times 0.30 \times 0.20 \text{ mm})$ was mounted on a glass fibre and low temperature data were collected on a Siemens SMART CCD area-detector 3-circle diffractometer (Mo Ka X-radiation, graphite monochromator, $\lambda = 0.710$ 73 Å). For three settings of φ , narrow data 'frames' were collected for 0.3° increments in ω . A total of 1271 frames of data were collected affording rather more than a hemisphere of data for the complex. At the end of data collection the first 50 frames of data were recollected to establish that crystal decay had not taken place during the course of data collection. The substantial redundancy in data allowed empirical absorption corrections to be applied using multiple measurements of equivalent reflections. Data frames were collected for 20 s per frame giving an overall time for data collection of ca. 12 h. The data frames were integrated using SAINT [10].

The structure was solved by conventional direct methods procedures and was refined by full-matrix least-squares on all F^2 data using Siemens SHELXTL 5.03 [10]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with isotropic thermal parameters ca. $1.2 \times$ the equivalent isotropic thermal parameters of their parent carbon atoms. The asymmetric unit contains two crystallographically independent molecules of the cation, four ClO_4^- anions and one molecule of MeCN. One of the ClO_4^- anions is disordered. All calculations were carried out on Silicon Graphics Indy or Indigo computers.

2.7.3. EXAFS studies

Extended X-ray absorption fine structure (EXAFS) spectroscopic measurements were performed at the Daresbury Synchroton Radiation Source (Daresbury Laboratory, Warrington, UK). Iron, cobalt, nickel and copper K-edge data were obtained on Station 8.1 using an order-sorting double crystal monochromator with focusing optics. Harmonic rejection was achieved by stepping off the peak of the rocking curve by 70% of the full height level. The monochromator was fitted with a Si(220) crystal which produced X-rays varying in energy from 5.5 to 11 KeV. Samples were prepared by pressing 13 mm pellets containing a mixture of complex (30-45 mg) and boron nitride (90-100 mg) and mounted in a cryogenically cooled aluminium holder. EXAFS were recorded at 293 and 77 K. Typically four or five data sets were collected for each complex and the analyses were carried out on the average spectra. Data analyses were performed using the program EX-CURV92 [24]. The programme performs least squares fitting of the EXAFS spectrum to a structural model with coordination numbers, radial distances (d) and Debye Waller factors as floating parameters. The errors in d are approximately ± 0.02 Å and in the coordination number $\pm 20\%$.

2.7.4. Electrochemistry

Cyclic voltammograms were performed under a dry dinitrogen atmosphere on 1 mM solutions of the complexes in dry deoxygenated acetonitrile containing 0.1 mol dm⁻³ NBu₄BF₄ as a supporting electrolyte, at scan rates of 50 to 500 mV s⁻¹. Then an equimolar amount of ferrocene was added as an internal standard.

3. Results and discussion

3.1. Synthesis and characterisation of L

Reaction of $PhP(CH_2CH_2SH)_2$ with 1,2-dichloroethane and Cs_2CO_3 under high dilution conditions affords L as an oil in reasonable yield (52%). This compares with yields of typically 35-40% for the analogous 9S3 preparation using S(CH₂CH₂SH)₂ with 1,2-dibromoethane and Cs₂CO₃. The macrocycle was characterised by elemental analysis, observation of a molecular ion in the mass spectrum (see Table 1) and by NMR spectroscopy. The ¹H and ¹H{³¹P} NMR spectra recorded at 600 MHz were sufficiently well resolved to allow simulation and iterative fitting using LAOCOON PC⁸ (see Section 2 and Fig. 1). The vicinal coupling constants (J 8.10, J' 2.83) for the S-C-C-S fragment are close to those calculated (J 8.18, J' 3.79) for a gauche equilibrium mixture as would be expected for a nine-membered ring [11]. Using the equations derived empirically by Abraham and Gatti [12], and applied by Lockhart and Tomkinson [11] to a range of thiamacrocycles, the expected values for the vicinal couplings in the P-C-C-S segments in a gauche equilibrium mixture are 8.64 and 4.28 Hz, close to the average of those observed (8.65 and 3.43 Hz). The observation of gauche placements does not, however, distinguish between exo- and endodentate conformations of L and therefore we undertook a molecular mechanics study to assess the likely geometry of L. Initially we modelled the phosphine sulfide c-PhPS-(CH₂CH₂S)₂CH₂CH₂, whose structure has been determined by X-ray crystallography [2], by starting from analogous conformations known for 9S3 [13]. Using the MM + force field in the HYPERCHEM package [9] (see Section 2) a minimum was found corresponding very closely to the crystallographically observed solid-state geometry, which is an exodentate conformation corresponding to the C₂ conformation of 9S3 [13]. A similar procedure for L produced an endodentate conformation corresponding to that observed in [Mo(CO)₃L] (Fig. 2(a)) as the lowest energy (16.61 kcal mol^{-1})

conformation. Exodentate conformations were found (Fig. 2(b)-(d)) at energies of 16.80, 17.28 and 17.91 kcal mol⁻¹, respectively. The results suggest that the endodentate conformation is preferred over exodentate conformations, which are however still ener-



Fig. 1. 1-phenyl-1-phospha-4,7-dithiacyclononane (L) showing the NMR labelling system.



Fig. 2. Local energy minima of L established using HYPERCHEM. (a) Endodentate 16.61 kcal mol⁻¹; (b) exodentate 16.80 kcal mol⁻¹; (c) exodentate 17.91 kcal mol⁻¹.

getically accessible, and that complexes of L would be expected to show high thermodynamic stability because there would be no enthalpy lost in conformationally adapting the ligand for facial coordination. Conformation Fig. 2(c) is similar to that observed in c-PhPS(CH₂CH₂S)₂CH₂CH₂ and Fig. 2(d) has been observed in [Cu(η^{1} -L)(η^{3} -L)][PF₆] (see above). Similar calculations with 9S3 suggest that the energy difference between endo- and exodentate conformations are even smaller (ca. 0.03 kcal mol⁻¹) [14].

3.2. Synthesis and structure of $[Cu(\eta^{1}-L)(\eta^{3}-L)][PF_{6}]$

Reaction of L with $[Cu(NCMe)_4][PF_6]$ affords $[Cu(\eta^1-L)(\eta^3-L)][PF_6]$ (1). The compound was characterised by X-ray crystallography (see Fig. 3 and Table 3). One equiv. of acetonitrile is incorporated in the crystal lattice. The complex is a distorted tetrahedron with one ligand facially tridentate and the other unidentate and coordinated via the phosphorus. A similar tetrahedral geometry has been observed for $[Cu(\eta^1-9S3)(\eta^3-9S3)][PF_6]$ in which one of the 9S3 ligands is unidentate [15,17]. The structure is also similar to



Fig. 3. The molecular structure of $[Cu(\eta^1-L)(\eta^3-L)]^+$ (1) showing the atom labelling system. Atoms are represented as 50% probability ellipsoids.

[Cu(9S3)(EPh₃)][ClO₄] (E = P, As) prepared by reaction of 9S3 with [Cu(NCMe)₄][ClO₄] in the presence of EPh₃ [16]. The η^3 -L has an endodentate conformation similar to that already established by X-ray crystallography in the structure of [Mo(CO)₃L]² and by molecular mechanics for the free ligand (Fig. 2(a)). The conformation of η^1 -L is similar to Fig. 2(d) found for the free

Table 3												
Selected	bond	lengths	(Å) a	nd	angles	(°)	for	[Cu(n	¹ -L)(n	³ -L)1	[PF₄]	(1)

Bond lengths (Å)			
Cu(1) - P(1)	2.246(3)	Cu(1)-S(1)	2.354(3)
Cu(1)–S(2)	2.366(4)	Cu(1)–P(2)	2.215(3)
P(1)–C(1)	1.842(12)	P(1)–C(6)	1.850(14)
P(1)–C(7)	1.818(15)	S(1)–C(2)	1.815(13)
S(1)–C(3)	1.828(15)	S(2)–C(4)	1.825(13)
S(2)–C(5)	1.836(13)	C(1)–C(2)	1.512(15)
C(3)–C(4)	1.509(20)	C(5)–C(6)	1.495(23)
P(2)-C(13)	1.853(10)	P(2)–C(18)	1.839(12)
P(2)-C(19)	1.832(12)	S(3)–C(14)	1.791(13)
S(3)-C(15)	1.820(17)	S(4)-C(16)	1.798(15)
S(4)-C(17)	1.817(15)	C(13)-C(14)	1.533(16)
C(15)-C(16)	1.495(21)	C(17)–C(18)	1.535(21)
Bond angles (°)			
P(1)-Cu(1)-S(1)	91.5(1)	P(1)-Cu(1)-S(2)	90.1(1)
S(1)–Cu(1)–S(2)	91.2(1)	P(1)-Cu(1)-P(2)	130.5(1)
S(1)-Cu(1)-P(2)	125.9(1)	S(2)-Cu(1)-P(2)	116.7(1)
Cu(1)-P(1)-C(1)	104.9(4)	Cu(1)-P(1)-C(6)	102.4(4)
C(1)–P(1)–C(6)	103.4(6)	Cu(1)-P(1)-C(7)	131.5(4)
C(1)–P(1)–C(7)	105.1(6)	C(6)-P(1)-C(7)	106.6(6)
Cu(1)-S(1)-C(2)	99.1(4)	Cu(1)-S(1)-C(3)	101.7(4)
C(2)–S(1)–C(3)	103.1(6)	Cu(1)-S(2)-C(4)	97.8(5)
Cu(1)–S(2)–C(5)	102.3(5)	C(4)-S(2)-C(5)	102.9(7)
Cu(1)-P(2)-C(13)	118.1(4)	Cu(1)–P(2)–C(18)	112.1(4)
C(13)–P(2)–C(18)	106.9(6)	Cu(1)–P(2)–C(19)	113.0(4)
C(13)–P(2)–C(19)	101.5(5)	C(18)–P(2)–C(19)	103.7(6)
C(14)-S(3)-C(15)	104.3(7)	C(16)-S(4)-C(17)	104.9(7)



Fig. 4. The molecular structure of $[HgL_2]^{2+}$ (2) (molecule 1) showing the atom labelling system. Atoms are represented as 40% probability ellipsoids.

ligand by molecular mechanics. The bite angles from the η^3 -L (average 90.9°) are substantially reduced from the values expected for a tetrahedral metal centre and are a consequence of the strained restricted conformation of L. The remaining angles at the copper centre are correspondingly larger (average 124.3°) and range from 130.5(1)° for P(1)-Cu(1)-P(2) to 116.7° for S(2)-Cu(1)-P(2) reflecting the steric interaction of the phenyl groups and the non-chelating part of η^1 -L. The steric crowding is also manifest in the large angle Cu(1)-P(1)-C(7) [131.5(4)°] and the orientation of the phenyl group attached to P(1) which is approximately co-planar with S(1), S(2) and P(1). When L is η^3 coordinated to a $Mo(CO)_3$ fragment the phenyl group is orientated perpendicular to the plane of the macrocycle; however, when in the more sterically congested seven-coordinate complex $[Mo(CO)_2Br_2(\eta^3-L)]$ the phenyl group adopts a co-planar orientation [2]. The Cu-S distances [average 2.360(4) Å] are longer than those observed in $[Cu(9S3)(AsPh_3)]^+$ [2.303(6) Å] $[16], [Cu(\eta^{1}-9S3)(\eta^{3}-9S3)]^{+} [2.316(7) \text{ Å}] [15] and$ $[Cu_2(9S3)_3]^{2+}$ [2.300 Å] [17]. Both the Cu-P distances are as expected with Cu(1)-P(1) being 0.032(3) Å longer than Cu(1)-P(2). The Cu-P distances are shorter than the Cu-S distances in accord with the greater σ -donor and π -acceptor abilities of phosphines compared with thioethers. The distance between Cu(1) and S(3) (3.546 Å) is too long to represent a significant interaction.

3.3. Synthesis and structure of $[HgL_2][ClO_4]_2$

Reaction of $Hg(ClO_4)_2$ with L affords $[HgL_2][ClO_4]_2$ (2) whose structure has been established by X-ray diffraction (Fig. 4 and Table 4). The asymmetric unit contains two independent cations which have essentially the same geometry, but are pseudo enantiomeric. It is interesting to compare the structure with that of $[Hg(9S3)_2][PF_6]_2$ which is approximately octahedral with two of the Hg–S bonds significantly shorter than the other four indicating a small tetragonal compression [18]. This structural feature was interpreted as a compromise between the third-row d¹⁰ metal ion's tendency to adopt linear coordination and the preference of 9S3 for facial binding. In $[Hg(9S3)_2]^{2+}$ the latter preference appears to dominate. The structure of **2** shows a much finer balance. The Hg–P bonds are short (average 2.404 Å) as is expected for a pseudo two-

Table 4

Selected bond lengths (Å) and angles (°) for $[HgL_2][ClO_4]_2 \cdot 1/2 \cdot (MeCN)$ (2)

	Molecule 1	Molecule 2
	(n = 1)	(n = 2)
Bond lengths (Å)		
Hg(n)-P(n11)	2.391(2)	2.4157(14)
Hg(n)-P(n31)	2.3940(14)	2.4151(14)
Hg(n)-S(n37)	3.055(2)	3.0587(14)
Hg(n)-S(n34)	3.082(2)	3.0590(14)
Hg(n)-S(n17)	3.109(2)	2.975(2)
Hg(n)-S(n14)	3.265(2)	3.131(2)
P(n11)-C(n12)	1.804(7)	1.816(6)
P(<i>n</i> 11)–C(<i>n</i> 21)	1.805(7)	1.806(6)
P(<i>n</i> 11)–C(<i>n</i> 19)	1.888(9)	1.822(6)
C(n12)-C(n13)	1.430(12)	1.530(8)
C(<i>n</i> 13)–S(<i>n</i> 14)	1.8269(8)	1.829(6)
S(<i>n</i> 14)–C(<i>n</i> 15)	1.797(9)	1.812(7)
C(n15)–C(n16)	1.404(13)	1.522(9)
C(<i>n</i> 16)–S(<i>n</i> 17)	1.839(10)	1.821(6)
S(<i>n</i> 17)–C(<i>n</i> 18)	1.765(10)	1.813(6)
C(<i>n</i> 18)–C(<i>n</i> 19)	1.419(14)	1.533(8)
P(<i>n</i> 31)–C(<i>n</i> 41)	1.796(6)	1.814(6)
P(<i>n</i> 31)–C(<i>n</i> 32)	1.822(6)	1.826(6)
P(<i>n</i> 31)–C(<i>n</i> 39)	1.832(6)	1.831(6)
C(<i>n</i> 32)–C(<i>n</i> 33)	1.534(8)	1.549(8)
C(n33)–S(n34)	1.825(6)	1.823(6)
S(n34)–C(n35)	1.814(7)	1.822(6)
C(n35)–C(n36)	1.536(9)	1.530(8)
C(<i>n</i> 36)–S(<i>n</i> 37)	1.821(6)	1.823(6)
S(<i>n</i> 37)–C(<i>n</i> 38)	1.815(7)	1.817(6)
C(n38)-C(n39)	1.539(9)	1.525(9)
Bond angles (°)		
P(n11)-Hg(n)-P(n31)	175.86(5)	164.84(5)
P(n11)-Hg(n)-S(n37)	98.83(5)	113.59(4)
P(n31)-Hg(n)-S(n37)	79.32(5)	78.57(4)
P(n11)-Hg(n)-S($n34$)	100.55(5)	99.94(4)
P(n31)-Hg(n)-S(n34)	75.35(4)	75.08(4)
S(n37)-Hg(n)- $S(n34)$	69.92(4)	69.94(6)
P(n11)-Hg(n)-S(n17)	75.26(6)	79.12(5)
P(n31)-Hg(n)-S(n17)	104.29(5)	115.16(5)
S(n37) - Hg(n) - S(n17)	147.80(5)	65.74(4)
S(n34) - Hg(n) - S(n17)	79.96(4)	130.49(4)
P(n11)-Hg(n)-S(n14)	73.42(5)	74.42(4)
P(n31)-Hg(n)-S(n14)	110.29(5)	105.14(5)
S(n37)-Hg(n)-S(n14)	143.06(4)	130.52(4)
S(n34)-Hg(n)-S(n14)	146.48(4)	159.50(5)
S(n17)-Hg(n)- $S(n14)$	66.56(5)	68.61(4)

Table 5 EXAFS data ^a

Shell	d	$2\sigma^{2 b}$	R °
	(Å)	(Å ²)	(%)
2P	2.216(4)	0.002(03)	20.0
2S	2.339(5)	0.004(06)	
6C	3.230(9)	0.018(2)	
2P	2.212(2)	0.007(03)	31.7
4S	2.356(3)	0.015(05)	
12C	3.308(6)	0.021(1)	
2P	2.220(2)	0.006(03)	31.0
4S	2.351(3)	0.017(06)	
12C	3.298(6)	0.021(2)	
2Br	4.187(13)	0.021(3)	
2P	2.266(5)	0.004(05)	23.8
4S	2.217(5)	0.011(09)	
12C	3.288(9)	0.023(3)	
	Shell 2P 2S 6C 2P 4S 12C 2P 4S 12C 2Br 2P 4S 12C	Shell d (Å)2P2.216(4)2S2.339(5)6C3.230(9)2P2.212(2)4S2.356(3)12C3.308(6)2P2.220(2)4S2.351(3)12C3.298(6)2Br4.187(13)2P2.266(5)4S2.217(5)12C3.288(9)	$\begin{array}{c cccc} {\rm Shell} & d & 2 \sigma^{2 \ \rm b} \\ ({\rm \AA}) & ({\rm \AA}^2) \\ \end{array} \\ \begin{array}{c} 2P & 2.216(4) & 0.002(03) \\ 2S & 2.339(5) & 0.004(06) \\ 6C & 3.230(9) & 0.018(2) \\ \end{array} \\ \begin{array}{c} 2P & 2.212(2) & 0.007(03) \\ 4S & 2.356(3) & 0.015(05) \\ 12C & 3.308(6) & 0.021(1) \\ \end{array} \\ \begin{array}{c} 2P & 2.220(2) & 0.006(03) \\ 4S & 2.351(3) & 0.017(06) \\ 12C & 3.298(6) & 0.021(2) \\ 2Br & 4.187(13) & 0.021(3) \\ \end{array} \\ \begin{array}{c} 2P & 2.266(5) & 0.004(05) \\ 4S & 2.217(5) & 0.011(09) \\ 12C & 3.288(9) & 0.023(3) \\ \end{array} $

^a Standard deviations in parentheses. Note that the systematic errors in bond distances arising from the data collection and analysis procedures are ca. 0.02–0.03 Å for well-defined coordination shells. ^b Debye–Waller factor.

^c *R* factor defined as $\left[\int (\chi^{T} - \chi^{E})k^{3} dk / \int \chi^{E}k^{3} dk\right] \times 100.$

coordinate complex and can be compared with a length of 2.389(5) Å found in $[Hg(tmpp)_2]^{2+}$ (tmpp = tris(2,4,6-trimethoxyphenyl)phosphine) [19]. The four Hg-S bond lengths (average 3.092 Å) are considerably longer than those in $[Hg(9S3)_2][PF_6]_2$ (average 2.693 Å). Similar weak interactions have been observed in 9S3 complexes of palladium(II) where the metal has a preference for square planar coordination [20]. For example, $[Pd(9S3)Br_2]$ has a long Pd-S distance of 3.125(1) Å. The structure suggests that L readily adopts an endodentate conformation even in the absence of a strong metal preference for facial coordination, consistent with the molecular mechanics results.

3.4. Synthesis of Ag, Ni, Co and Fe complexes

Reaction of L with $AgBF_4$, $Ni(BF_4)_2$, $CoBr_2$ and $Fe(BF_4)_2$ affords $[AgL_2][BF_4]$ (3), $[NiL_2][BF_4]_2$ (4), $[CoL_2]Br_2$ (5), $[FeL_2][BF_4]_2$ (6), respectively, which were characterised by FAB mass spectroscopy and elemental analysis (Table 1), but unfortunately we were not able to obtain single crystals suitable for X-ray diffraction.

3.4.1. EXAFS

Further structure information for complexes 4, 5 and 6 was obtained by EXAFS. Data were recorded at 293 and 77 K, but in all cases the low temperature data was superior and is summarised in Table 5. This was particularly noticeable for 4 and 5 where the phosphorus and sulfur shells were resolved at 77 K, but not at 293 K. Initial studies were performed on 1 where single crystal data is available for comparison. In the initial fitting of

the EXAFS the coordination numbers were allowed to float. The values obtained were within 20% of the crystallographic coordination numbers and therefore further analyses were undertaken with these latter values. A similar approach was taken for the EXAFS of 4, 5 and 6. The best fit (R = 20%) for 1 was obtained for a model analogous to the X-ray structure with a first shell comprising of two phosphorus atoms (2.216 Å) and two sulfur atoms (2.339 Å) and a second shell of six carbon atoms (3.230 Å).

Three distinct shells are observed for **4** corresponding to phosphorus, sulfur and carbon as shown in Fig. 5(a). The phosphorus shell at 2.212 Å compares well with the average Ni–P distance of 2.201 Å obtained for nickel phosphine complexes in the Cambridge Crystallographic Database [21]. The sulfur shell at 2.356 Å is in accord with the average Ni–S distance in $[Ni(9S3)_2]^{2+}$ (2.386 Å) [22]. The complex is therefore six-coordinate and probably a distorted octahedron of more regular symmetry than **2**.

Four distinct shells are observed for **5** corresponding to phosphorus, sulfur, carbon and bromine as illustrated in Fig. 5(b). Again the complex is six-coordinate with the phosphorus shell at 2.220 Å being close to that expected from the average Co–P distance of 2.223 Å for cobalt phosphine complexes in the Cambridge Crys-



Fig. 5. (a) Fourier transformed nickel K-edge EXAFS spectrum of $[NiL_2][BF_4]_2$ (4) (full line: experimental, broken line: theory). (b) Fourier transformed cobalt K-edge EXAFS spectrum of $[CoL_2]Br_2$ (5) (full line: experimental, broken line: theory).

Table 6 Electronic spectroscopy data for complexes of L and 9S3 [23]

Complex	$\lambda \text{ (nm) } (\epsilon \text{ (dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}))$	Solvent
$[NiL_2]^{2+}$ (4)	675 (98), 317 (16434), 200 (42155)	H ₂ O
$[Ni(9S3)_2]^{2+}$	784 (27), 527 (26), 325 (14000)	H_2O
$[CoL_2]^{2+}$ (5)	327 (14147), 264 (11750), 200 (43603)	H_2O
$[Co(9S3)_2]^{2+}$	730 (11), 560 (sh), 480 (92), 338 (6600), 264 (6500)	MeCN
$[FeL_2]^{2+}$ (6)	480 (308), 375 (259), 275 (17470), 211 (26272)	MeCN
$[Fe(9S3)_2]^{2+}$	523 (53), 395 (52)	H_2O

tallographic Database. The sulfur shell distance of 2.351 Å is similar to the average Co–S distance (2.321 Å) in $[Co(9S3)_2]^{2+}$ [22].

Even at low temperature distinct phosphorus and sulfur shells were not resolved for 6. This is not surprising since average Fe–S and Fe–P distances for iron thioether and iron phosphine complexes obtained for the Cambridge Crystallographic Database are very similar (2.273 and 2.247 Å). Again EXAFS confirms the presence of a six-coordinate complex.

3.5. Electronic spectroscopy

The electronic spectra of **4**, **5** and **6** were recorded (see Table 6) and all have intense absorptions below 250 nm due to the phenyl rings. The spectrum of **4** contains a band at 675 nm ($\varepsilon = 98$) assigned to the d-d transition ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$, characteristic of a Ni²⁺ ion in a pseudo-octahedral environment, and a higher energy transition at 317 nm ($\varepsilon = 16434$) assigned to the ${}^{3}A_{2g} \rightarrow$ ${}^{3}T_{1g}(F)$ transition overlapping with a charge-transfer band. The increase in transition energies and extinction coefficients compared with the analogous 9S3 derivative (Table 6) indicates that L is a stronger field ligand ($\mathcal{A}_{o} = 14810$ versus 12760 cm⁻¹) and that, as expected, the L complex is of lower symmetry.

Complex **6** has two d-d absorption maxima typical of low spin Fe(II) in a pseudo-octahedral field corresponding to ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ which are not obscured by intense charge-transfer bands. From the energy difference of these two maxima, which is approximately 16*B*, and assuming C = 4B, Δ_{o} is calculated to be 22290 cm⁻¹ and B = 364 cm⁻¹ [23].

 ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g} = \varDelta_{o} - C$ ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g} = \varDelta_{o} + 16B - C$

For $[Fe(9S3)_2]^2 + \Delta_0$ is 20670 cm⁻¹ and B = 387 cm⁻¹. In the spectrum of the Co²⁺ complex **5** no d-d bands were observed, presumably due to the high intensity charge-transfer bands tailing off into the low energy region of the spectrum.

Table 7 Cyclic voltammetry data for complexes of L and 9S3 [23]

Complex	Couple	$E_{1/2}$ (V)	Rev/Irrev
$[NiL_2]^{2+}$ (4)	${{Ni^{2+}/Ni^{3+}}\over {Ni^{2+}/Ni^+}\over {Ni^+/Ni^0}}$	$+0.22 \\ -0.99 \\ -1.43$	Rev Rev Rev
$[Ni(9S3)_2]^{2+}$	${Ni^{2+}/Ni^{3+}\over Ni^{2+}/Ni^{+}}$	$+0.97 \\ -1.07$	Rev Irrev
$[CoL_2]^{2+}$ (5)	$\mathrm{Co}^{2+}/\mathrm{Co}^{3+}$	-0.17	Rev
$[Co(9S3)_2]^{2+}$	$\begin{array}{c} Co^{2+}/Co^{3+} \\ Co^{2+}/Co^{+} \end{array}$	$-0.013 \\ -0.86$	Rev Rev
$[FeL_2]^{2+}$ (6)	$\mathrm{F}\mathrm{e}^{2+}/\mathrm{F}\mathrm{e}^{3+}$	+0.96	Rev
[Fe(9S3) ₂] ²⁺	$\mathrm{F}\mathrm{e}^{2+}/\mathrm{F}\mathrm{e}^{3+}$	+0.98	Rev



Fig. 6. Cyclic voltammogram of [NiL₂][BF₄]₂ (4).

3.6. Electrochemistry

Electrochemical data for the complexes and of analogous 9S3 complexes are shown in Table 7. These studies were undertaken to determine whether or not substitution of a thioether donor by a phosphine donor would render the complexes easier to oxidise (as a result of the greater σ -donor capacity of the phosphine), or easier to reduce (as a consequence of the greater π -acceptor capacity of the phosphine). In the case of the Ni(II) complex 4 (Fig. 6) both effects seem to operate with the complex being both easier to oxidise to Ni(III) and reduce to Ni(I) than its 9S3 analogue. Additionally in the case of 4 the Ni(0) state is reversibly accessible, thus L has the ability to stabilise Ni in four oxidation states. The differences for the Fe and Co complexes are less pronounced.

4. Conclusions

We can conclude that the structural studies confirm that the conformational preferences of L can be predicted by reference to the known behaviour of 9S3. L can coordinate in a facial, tridentate manner, and where this is precluded by the stereochemical preferences of the metal [e.g. Cu(I)], the exodentate conformation of L matches that of 9S3 on the related Cu complex. The structure of $[HgL_2]^{2+}$ suggests that even very weak metal-thioether bonding influences are sufficient to enforce an endodentate conformation. This view is supported by molecular mechanics calculations that suggest that L prefers the endodentate conformation to a greater extent than 9S3. The nine-membered ring topology therefore offers a good prospect for development of powerful ligating systems for soft metals.

Acknowledgements

We thank the EPSRC and the Cancer Research Campaign for studentships (S.N.S., G.E.D.M. and R.J.S.) and the EPSRC for access to the mass spectrometry, NMR and Chemical Database (D.A. Fletcher, R.F. McMeeking, D. Parkin, J. Chem. Int. Comput. Sci., 36 (1996) 746) services and the Synchrotron Radiation Source at the Daresbury Laboratory. We thank Dr R.E. Benfield for assistance in collecting the EXAFS data.

References

- R.J. Smith, A.K. Powell, N. Barnard, J.R. Dilworth, P.J. Blower, J. Chem. Soc., Chem. Commun. (1993) 54.
- [2] P.J. Blower, J.C. Jeffery, J.R. Miller, S.N. Salek, D. Schmaljohann, R.J. Smith, M.J. Went, Inorg. Chem. 36 (1997) 1578.

- [3] S.G. Murray, F.R. Hartley, Chem. Rev. 81 (1981) 365.
- [4] A.J. Blake, M. Schröder, Adv. Inorg. Chem. 35 (1990) 1.
- [5] S.R. Cooper, S.C. Rawle, Struct. Bonding (Berlin) 72 (1990) 1.
- [6] P.G. Edwards, J.S. Fleming, S.S. Liyanage, S.J. Coles, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1996) 1801.
- [7] P.J. Blower, J.R. Dilworth, G.J. Leigh, B.D. Neaves, F.B. Normanton, J. Hutchinson, J.A. Zubieta, J. Chem. Soc., Dalton Trans. (1985) 2647.
- [8] M. Clark, J.S. Thrasher, J. Chem. Educ. 67 (1990) 235.
- [9] J.L. Pazun, J. Chem. Inf. Comput. Sci. 33 (1993) 931.
- [10] Siemens Analytical Instruments, Madison, WI, USA.
- [11] J.C. Lockhart, N.P. Tomkinson, J. Chem. Soc., Perkin Trans. 2 (1992) 533.
- [12] R.J. Abraham, G. Gatti, J. Chem. Soc. B (1969) 961.
- [13] R. Bloom, D.W.H. Rankin, H.E. Robertson, M. Schröder, A. Taylor, J. Chem. Soc., Perkin Trans. 2 (1991) 773.
- [14] R.J. Smith, S.N. Salek, M.J. Went, P.J. Blower, N.J. Barnard, J. Chem. Soc., Dalton Trans. (1994) 3165.
- [15] S.K. Kano, R.S. Glass, G.S. Wilson, J. Am. Chem. Soc. 115 (1993) 592.
- [16] A.J. Blake, R.O. Gould, A.J. Holder, A.J. Lavery, M. Schröder, Polyhedron 9 (1990) 2919.
- [17] J.A. Clarkson, R. Yagbasan, P.J. Blower, S.R. Cooper, J. Chem. Soc., Chem. Commun. (1989) 1244.
- [18] A.J. Blake, A.J. Holder, T.I. Hyde, G. Reid, M. Schröder, Polyhedron 8 (1989) 2041.
- [19] L.-J. Baker, G.A. Bowmaker, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1993) 3235.
- [20] K. Wieghardt, H.-J. Küppers, E. Raabe, C. Krüger, Angew. Chem., Int. Ed. Engl. 25 (1986) 1101.
- [21] F.H. Allen, O. Kennard, Chem. Design Autom. News, 8 (1993) 1 and 31.
- [22] W.N. Setzer, C.A. Ogle, G.S. Wilson, R.S. Glass, Inorg. Chem. 22 (1983) 266.
- [23] K. Wieghardt, H.-J. Küppers, J. Weiss, Inorg. Chem. 24 (1985) 3067.
- [24] N. Binsted, J.W. Campbell, S.J. Gurman, P.C. Stephenson, EXCURV92, SERC Daresbury Laboratory, 1992.