Structural, spectroscopic and magnetic properties of $M[R_2P(E)NP(E)R'_2]_2$ complexes, M = Co, Mn, E = S, Se and R, R' = Ph or ⁱPr. Covalency of M–S bonds from experimental data and theoretical calculations[†][‡]

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The S/Se-containing bidentate ligands LH of the type $R_2P(E)NHP(E)R'_2$, E = S, Se and R, R' = Ph or ⁱPr have been employed to synthesize ML_2 (M = Mn, Co) complexes which contain the biologically important MS_4 core. Theoretical calculations on the LH and L⁻ forms of the ligands probe the geometric and electronic changes induced by the deprotonation of the LH form, which are correlated with structural data from X-ray crystallography. These results reflect the flexibility of the ligands, which enables them to be rather versatile with respect to the formation of ML₂ complexes with varied geometries and MEPNPE metallacycle conformations. A series of old and new ML₂ complexes have been synthesized and their structural, spectroscopic and magnetic properties characterized in detail. The nephelauxetic ratio β of the CoL₂ complexes provides evidence of covalent interactions, whereas the EPR properties of the MnL_2 complexes are interpreted on the basis of predominant ionic interactions, between the metal center and the ligands, respectively. Additional evidence for the existence of covalent interactions in the CoL₂ complexes (R = Ph, ⁱPr, or mixed Ph/ⁱPr), is offered by comparisons between their ³¹P NMR. The aforementioned notations are supported by extensive theoretical calculations on the ML₂ (E = S, R = Me) modelled structures, which probe the covalent and ionic character of the M–S bonds when M = Co or Mn. Wider implications of the findings of the present study on the M–S covalency and its importance in the active sites of various metalloenzymes are also discussed.

Introduction

Extensive crystallographic studies during the last few years have revealed the existence of M-S bonds in the active site of many metalloenzymes, involving either sulfide ions (S²⁻), Cys-thiolate, Met-thioether, or dithiolenic moieties, most prominently with the transition metals M = Fe, Ni, Cu, Zn, Mo, W¹ In this respect, beyond the above metals, one should also consider Co, since it has recently been shown that the enzyme ATP sulfurylase is a metalloenzyme containing Co(II) and Zn(II) in its active site, with the metal ion bound possibly to three S(Cys) and one N(His) residues.² In addition, the active site of the enzyme nitrile reductase contains either Fe(III) or Co(III), coordinated to posttranslationally oxidized Cys ligands,³ that has been modelled by a wealth of small complexes.⁴ Moreover, due to the lack of spectroscopic and magnetic properties of Zn(II)-containing enzyme active sites, Zn-enzymes, like alcohol dehydrogenase, or "Zn-fingers", are frequently reconstituted by Co(II), with the formation of S(Cys)rich coordination spheres around Co(II).⁵ Analogous Co(II)S₄

centers have been obtained by the reconstitution of the $FeS(Cys)_4$ protein rubredoxin by Co(II),⁶ or the coordination of Co(II) to the Cys-rich Zn- or Cd-metallothioneins.⁷ The coordination of Co(II) to S-containing ligands has also been achieved in small peptides or "maquettes", which retain critical structural and spectroscopic properties of analogous Co(II) biological sites.⁸

On the other hand, Mn(II) is not coordinated to S-containing amino acids in biological sites, while it prefers O- and Ncontaining biological ligands.⁹ It should be stressed, however, that Mn is extensively coordinated to sulfides, as for example, in the organometallic complexes reviewed recently.¹⁰

Our research groups are interested in the synthesis of complexes of certain first-series transition elements, with S/Se-containing bidentate ligands LH of the type $R_2P(E)NHP(E)R'_2$, E = S or Se. These ligands are considered to be inorganic analogues of β -diketonates, since deprotonation is always accommodated by an extensive delocalization of π electronic density, a phenomenon verified by X-ray crystallography and spectroscopic data.^{11,12} A wealth of ML₂ complexes have been synthesized and thoroughly characterized in the past, with the reported examples involving numerous main-group, as well as transition elements.¹¹ The interest in metal complexes containing ligands of this type stems mainly from the structural flexibility of the deprotonated forms (L^{-}) , since (i) proper selection of the R, R' groups leads to symmetrical (R = R') or asymmetrical coordination spheres $(R \neq R')$, and (ii) MEPNPE metallacycles adopt either pseudo-chair or pseudoboat conformations, depending on the metal and the peripheral R groups.12b

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[†] Fig. 1 in colour; Tables S1–S2; Fig. S1–S6.

[‡] In memoriam to Professor Andreas T. Tsatsas.

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The structural flexibility of the ligands is explored in the present work by theoretical calculations, which probe the structural and electronic changes induced by deprotonation of the ligands, as well as by their coordination to a metal ion.

The second important feature of these ligands is their large $E \cdots E$ "bite" (*ca.* 4 Å), which induces less strain in the metal–ligand ring and, therefore, allows them to accommodate the requirements of various metal-coordination geometries.^{11,12b} Thus, there is a range of observed geometries, some of which are characteristically distorted from ideal ones and confer specific electronic properties to the MS₄ core, that might resemble those of the active site of certain metalloenzymes. Such a case, involving the study of distorted tetrahedral or square planar¹³ Ni[R₂P(S)NP(S)R'₂]₂ (R, R' = Ph or ⁱPr) complexes, is currently under experimental and theoretical investigation, (P. Kyritsis, N. Robertson *et al.*, unpublished), in order to address critical questions on the electronic properties of NiS₄-containing metalloenzyme active sites, like hydrogenase and CO dehydrogenase.¹⁴

In addition to the theoretical study of the ligands, the synthesis and characterization of the following new ML₂ complexes $Co[^{i}Pr_{2}P(S)NP(S)Ph_{2}]_{2}$ (3), $Mn[^{i}Pr_{2}P(S)NP(S)^{i}Pr_{2}]_{2}$ (5), $Mn[^{i}Pr_{2}P(S)NP(S)Ph_{2}]_{2}$ (6) and $Mn[Ph_{2}P(Se)NP(Se)Ph_{2}]_{2}$ (7) is described. The structures of these complexes have been determined by X-ray crystallography. Moreover, the previously reported complexes $Co[Ph_2P(S)NP(S)Ph_2]_2$ (1), $Co[^iPr_2P(S)NP(S)^iPr_2]_2$ (2), $Mn[Ph_2P(S)NP(S)Ph_2]_2$ (4), and $Zn[Ph_2P(S)NP(S)Ph_2]_2$ (8) have also been prepared. The whole set of complexes have been studied by spectroscopic methods (1H and 31P NMR, IR, UV-VIS, EPR), and their magnetic properties investigated by magnetisation measurements between 350 and 2 K. All complexes studied have been crystallized in a tetrahedral or pseudo-tetrahedral geometry. The tetrahedral nature of the complexes examined in this study is of interest from a magnetic point of view, since all complexes are typically high-spin and paramagnetic. The structural, spectroscopic and magnetic properties of these MS₄containing complexes (M = Mn, Co), combined with the results of appropriate theoretical calculations, are discussed with respect to the relative covalency of their M-S bonds. This feature is often discussed in the case of Cu-S, Fe-S and Ni-S containing proteins,¹⁵ but has not yet been extensively studied in the case of Co-S containing enzymes or "maquettes".

Experimental

Materials and instrumentation

UV-VIS, IR and NMR spectroscopy. IR spectra were run in the range 4000–200 cm⁻¹ on a Perkin-Elmer 883 IR spectrophotometer, as KBR discs. ¹H and ³¹P spectra were recorded in a Varian Unity Plus 300 MHz instrument. The ¹H and ³¹P chemical shifts are relative to SiMe₄ and 85% H₃PO₄, respectively. Electronic spectra were recorded on a Cary 300 Varian spectrophotometer and a Perkin-Elmer Lamda 9 spectrophotometer.

Magnetic susceptibility studies. Magnetic susceptibility measurements were carried out between 2 K and 300 K, using a Quantum design MPMS2 SQUID magnetometer with MPMS MultiVu Application software to process the data. The magnetic field employed was 0.1 T.

EPR spectroscopy. EPR measurements were carried out at 77 K on an X-band Bruker ER200D-SCR spectrometer, connected to a Datalink 486DX PC running EPR Acquisition System, version 2.42 software.

X-Ray crystallography. X-Ray diffraction intensities were collected with Mo-K α radiation on a Bruker Smart APEX CCD diffractometer equipped with an Oxford Cryosystems low-temperature device operating at 150 K. Absorption corrections were carried out with the multiscan procedure SADABS.¹⁶ The structure was solved by direct methods (SHELXS97)¹⁷ and refined by full-matrix least squares against $|F|^2$ using all data (SHELXL97).¹⁸ H-atoms were placed in calculated positions and allowed to ride on their parent atoms. All non H-atoms were modelled with anisotropic displacement parameters. The crystallographic data of our studies are shown in the ESI†.

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Theoretical calculations. Ground-state electronic structure calculations have been performed using Density Functional Theory (DFT) methods, by employing the Gaussian 98 software package.¹⁹ The hybrid (HF/DFT) Density Functional B3LYP was applied, which consists of the non local hybrid exchange functional, as defined by Becke's three parameters equation and the non local Lee-Yang-Parr correlation functional.²⁰ For the Co and Mn metal centers, the SDD²¹ effective core potential was applied, whereas for all non-metal centers, the triple-ζ6-311G* basis set with p-type polarization function was used.²² The electronic ground-state was left to full geometry optimization without any symmetry constraint, starting either from the crystallographic structures or from built models when the crystallographic coordinates were not available. The density matrix in geometry optimization energy calculations was converged to a tight root mean square threshold of 10⁻⁸ au. The optimum structure, located as a saddle point of the potential energy, was verified by the absence of imaginary frequencies. The derived wave functions were found free of internal instabilities. The estimation of the Atomic Orbitals (AOs) contribution in Molecular Orbitals (MOs) of the complexes, as well as the Overlap Population Analysis (OPA), were performed with the AOMix software.23 The analysis of the MO compositions in terms of fragment molecular orbitals, the construction of orbital interaction diagrams, as well as the charge decomposition analysis was performed using AOMix-CDA.23a The chemical bonding in the complexes, at the B3LYP optimized ground state geometries, was also studied by Natural Bond Orbital (NBO)²⁴ analysis of the appropriate density matrix, by B3LYP single point calculations. Quantitative analysis of the NBOs, as well as the corresponding Natural Atomic Orbitals (NAOs) and the Natural Localized Molecular Orbitals (NLMOs) was also applied, in order to estimate bond covalencies. Determination of the Natural Population Analysis NLMO/NPA bond orders was computed using the NAOs of the NLMOs, and the sign of these values is obtained from the overlap integrals of Natural Hybrid Orbitals (NHOs), located on the covalently bonded atoms.25 All NBO calculations were performed with the NBO 5.0 software package, whereas the NBOView 1.0 software was used for the visualization of the NBOs and their corresponding NLMOs.26 The visualization of the Kohn-Sham MOs was performed by the Molekel 3.4 software.²⁷

Synthesis

All manipulations were carried out under a pure Ar atmosphere, unless otherwise mentioned. All chemical reagents used were purchased from Aldrich. The LH ligands Ph₂P(S)NHP(S)Ph₂ (^{Ph}LH),²⁸ ⁱPr₂P(S)NHP(S)ⁱPr₂ (^{iPr}LH),²⁹ ⁱPr₂P(S)NHP(S)Ph₂ (^{iPr,Ph}LH),³⁰ Ph₂P(Se)NHP(Se)Ph₂,³¹ their corresponding KL salts, as well as complexes 1,³² 2,³² 4,³³ and 8,³⁴ were prepared according to published procedures.

Co['**Pr**₂**P**(**S**)**NP**(**S**)**Ph**₂]₂ (3). In a Schlenck-type flask were added 20 mL CH₃OH and 0.21 g (0.5 mmol) K['**P**r₂**P**(**S**)**NP**(**S**)**Ph**₂]. The mixture was stirred at room temperature for 30 min, and subsequently 0.059 g (0.25 mmol) CoCl₂·6H₂O were added. The mixture was stirred for 2 h and during that time a solid blue product was formed, which was collected by filtration. The product (yield 68%) was crystallized by slow mixing of an acetone solution of the complex and methanol (1 : 3), affording blue needle-like crystals, which were suitable for X-ray crystallography. IR (cm⁻¹) ν (Ph₂P–S) 573 s, ν ('**P**r₂P–S) 527 s, ν (PNP) 1231br; $\delta_{\rm H}$ (CDCl₃) 1.49 [4H, s, CH], 4.75 [8H, br, *m*-C₆H₅], 6.03 [4H, d, ⁵*J*(PH) = 58.18 Hz, *p*-C₆H₅], 7.77 [12H, d, ³*J*(PH) = 123.49 Hz, CH₃], 8.41 [8H, d, ³*J*(PH) = 141.25 Hz, *o*-C₆H₅], 9.45 [12H, s(br), CH₃]; $\delta_{\rm P}$ (CDCl₃) – 87.8 [s(br), Ph₂P], –188.4 [s(br), '**P**r₂P]

Mn[ⁱ**Pr**₂**P**(**S**)**NP**(**S**)ⁱ**Pr**₂]₂ (5). In a Schlenck-type flask were added 20 mL CH₃OH, 0.15 g (0.5 mmol) ⁱ**Pr**₂**P**(**S**)**NHP**(**S**)ⁱ**Pr**₂ and 0.056 g (0.5 mmol) potassium butoxide (C₄H₉OK), in order to deprotonate *in situ* the ligand. The mixture was stirred at room temperature for 30 min, and subsequently 0.049 g (0.25 mmol) MnCl₂·6H₂O were added. The mixture was stirred for 2 h and during that time a solid pale pink product was formed, which was collected by filtration. The product (yield 86%) was crystallized by slow mixing of a CH₂Cl₂ solution of the complex and hexane, affording pink cuboidal crystals, which were suitable for X-ray crystallography. IR (cm⁻¹) ν (PS) 549 m, ν (PNP) 1223br.

Mn[ⁱ**Pr**₂**P**(**S**)**NP**(**S**)**Ph**₂]₂ (6). In a Schlenck-type flask were added 20 mL CH₃OH and 0.21 g (0.5 mmol) K[ⁱ**Pr**₂**P**(**S**)**NP**(**S**)**Ph**₂]. The mixture was stirred at room temperature for 30 min and subsequently 0.058 g (0.25 mmol) MnCl₂·6H₂O were added. The mixture was stirred for 2 h and during that time a solid pale pink product was formed, which was collected by filtration. The product (yield 85%) was crystallized by slow mixing of a CH₂Cl₂ solution of the complex and hexane, affording pink cuboidal crystals, which were suitable for X-ray crystallography. IR (cm⁻¹) ν (Ph₂P–S) 576 s, ν (ⁱPr₂P–S) 528 s, ν (PNP) 1233br.

 $Mn[Ph_2P(Se)NP(Se)Ph_2]_2$ (7). In a Schlenck-type flask were added 20 mL CH₃OH and 0.21 g (0.5 mmol) K[Ph₂P(Se)-NP(Se)Ph₂]. The mixture was stirred at room temperature for 30 min, and subsequently 0.058 g (0.25 mmol) MnCl₂·6H₂O were added. The mixture was stirred for 2 h and during that time a solid pale pink product was formed, which was collected by filtration. The product (yield 85%) was crystallized by slow mixing of a CH₂Cl₂ solution of the complex and hexane, affording pink cuboidal crystals, which were suitable for X-ray crystallography. IR (cm⁻¹) $v(Ph_2P$ -Se) 536 s, v(PNP) 1205br.

Results and discussion

Theoretical calculations on the ligands LH and \mathbf{L}^{-}

In the past, DFT calculations were performed on models of LH forms of the ligands, in which the peripheral R groups were replaced by H atoms.³⁵ However, to the best of our knoweledge, up to now there has been no detailed theoretical study on the delocalization of π electronic density³⁶ and its effect on the structural and electronic characteristics of this family of ligands.

The existence of a small degree of π electronic delocalization even in the LH forms, has already been noticed, demonstrated by the P–N bond lengths that are between those of single and double bonds, as well as the very small degree of pyramidalisation at the N atom.^{12,31}

In order to investigate the increase of the delocalization of π electronic density upon deprotonation of LH, as well as its influence on bond lengths and angles, DFT calculations were performed on the LH and L⁻ forms of the following four ligands (Fig. 1): Me₂P(S)NHP(S)Me₂ (^{Mc}LH),³⁷ P^hLH,³⁸ i^prLH,²⁹ and i^pr,^{ph}LH,³⁰ starting from the published crystallographic coordinates. Taking into consideration the existence of the ligand ion P^hL⁻ in two different geometries, depending on the counter cation,^{12a,39} the L⁻ forms were produced from the corresponding LH forms by substracting the N-proton and then leaving the structure to fully optimize its geometry, with tight criteria of convergence. The aim was to investigate the effects of the additional N lone pair (LP)⁴⁰ that is created upon deprotonation, on the structural and electronic properties of the ligands.

All ligands were optimized in C_1 symmetry without any constraint criteria. As can be seen from the data in Table 1, the optimized structures of the LH ligands are in excellent agreement with the corresponding X-ray structures, since the differences are in the accepted limits for a B3LYP level DFT calculation. Upon deprotonation of the LH forms, there are changes in the following three structural features:

Table 1 Selected structural properties from the crystal structures (exp) and the optimized geometries (calc) of the LH and L^- forms of the ligands

R = Ph/Me,	Me	LH	Me L-	^{iPr} I	H	^{iPr} L ⁻	iPr,Ph	LH	$^{\mathrm{i}Pr,Ph}L^{-}$	$^{\rm Ph}{ m I}$.H	$^{\rm Ph}{\rm L}^-$
$\mathbf{R}' = {}^{\mathrm{i}}\mathbf{P}\mathbf{r}$	exp	calc	calc	exp	calc	calc	exp	calc	calc	exp	calc	calc
av. P(R)–S/Å	1.950	1.966	2.017				1.936	1.962	2.013	1.919	1.971	2.011
av. P(R′)–S/Å				1.947	1.973	2.023	1.948	1.968	2.016			
av. P(R)–N/Å	1.678	1.718	1.610				1.674	1.721	1.602	1.670	1.718	1.587
av. P(R')–N/Å				1.688	1.738	1.615	1.703	1.737	1.621			
av. N–H/Å	0.894	1.015		0.975	1.019		1.075	1.013			1.015	
av. P–N–P/°	133.2	134.8	137.1	130.7	134.5	141.0	129.5	130.4	141.5	131.7	136.8	159.3
av. P–S–N/°	110.9	112.1	118.5	114.6	116.1	119.9	114.8	115.9	120.7	115.7	114.9	118.6



Fig. 1 Ground state optimized structures of the LH and L⁻ forms of the ligands, as well as of complexes 11 and 12.

(a) P–S and P–N bond lengths. In the optimized structures of all ligand ions (L⁻) mentioned above and presented in Fig. 1, the P–S bonds are lengthened, whereas the P–N bonds are shortened, compared to the corresponding LH forms (Table 1), a feature strongly correlated to π delocalization. Therefore, it is confirmed that deprotonation of the ligands is the prime factor that enhances π delocalization along the EPNPE fragment.

(b) Enlargement of the P–N–P angles. Electronic delocalization has also been considered to affect the magnitude of the P–N–P angles. In the crystal structure of $^{Ph}L^-$ with bis (triphenylphosphine) iminium as the counter cation, a linear P–N–P fragment has been observed.^{12a} Theoretical calculations, presented below, demonstrate the opening of the P–N–P angle as a result of deprotonation, in the absence of any counter cation.

In the case of ^{iPr}L⁻ and ^{iPr,Ph}L⁻, the P–N–P angle is increased from 134.5° and 130.4° in the LH form, to 141.0° and 141.5° in the L⁻ form, respectively, whereas in ^{Me}L⁻ the P–N–P angle remains almost unchanged, compared to the corresponding LH form. These values are typical of the P–N–P angles observed in previously reported pseudo-tetrahedral ML₂ complexes containing these ligands,^{29,32,37} as well as the complexes **3** and **6**. In the case of ^{Ph}L⁻, the P–N–P angle (159.3°) approaches linearity even further. These observations will be further discussed below with respect to pyramidalisation effects.

In the majority of the ML₂ complexes, the P–N–P angle varies between 132° and 142°, depending on the R groups attached to P atoms.^{11,12b} Therefore, it is mainly deprotonation, accompanied by an increase of π delocalization, that should be considered as the main reason for the enlargement of P–N–P angles upon the formation of the ML₂ complexes. This proposal is also supported by theoretical calculations on the M^{Me}L₂ complexes (M = Co, Mn), described in the following paragraphs.

(c) Angles between the P–S–N planes. Another characteristic structural feature of the LH forms is the relative positions of the P–S–N planes. This has already been described for a series of LH ligands in terms of *anti* or *syn* conformations, in which the S–P···P–S torsion angles are $150-180^{\circ}$ and $<90^{\circ}$, respectively.^{11c} The factor that decides which structure is adopted by a given LH ligand, is the nature of the peripheral R groups. It is of interest to note that according to published crystallographic data, all ligands containing the SPNPS fragment adopt the *anti* conformation, which seems to be energetically favourable, except for those possessing ¹Pr groups, which adopt the *syn* conformation.^{11c} This trend is also observed in our theoretical calculations, for both the protonated and deprotonated forms of the ligands. It should be stressed that

upon deprotonation, the ligands that possess ⁱPr groups retain their *syn* conformation, whereas all others adopt the *anti* one. This shows that in the absence of a counter cation, the values of the S–P···P–S torsion angles are mainly affected by the steric effects of the R groups. Therefore, flexibility of the system when R = Me (small size),³⁷ Ph (planar),³⁸ or even Bu (freedom of rotation),⁴¹ results in large torsion angles, which is not the case when the ligand possesses the bulky and not easily rotated ⁱPr groups.^{29,30}

Trends in π delocalization among the LH and L^- forms

(a) Pyramidalisation effects in the LH and L⁻ forms. The low degree of pyramidalisation of the N atom has been considered as evidence that π electron delocalization already exists in the LH forms.^{12,31} The crystal structures of ^{iPr,Ph}LH³⁰ and ^{Ph}LH³⁸ show that the N atom lies between 0.18 Å and 0.22 Å out of the plane of its substituents (sum of bond angles close to 360°), whereas in the case of ^{Me}LH,³⁷ both P atoms, N and H are coplanar (sum of bond angles 360° exactly), indicating close to sp² and sp² hybridization of N, respectively. It should be noted that in the crystal structure of ^{iPr}LH,²⁹ no pyramidalisation of N is observed, since both P atoms, N and H lie in the same plane. However, our theoretical analysis reveals that the N atom lies 0.21 Å out of the plane of its substituents. The planarity observed in the crystal structure may be due to packing interactions and hydrogen bonding.

By calculating the NHO compositions of N atom character in the P–N bonds for the LH forms, we predict an $sp^{1.7-1.9}$ hybridization for N, thus explaining the near planarity of the three bonds (both P–N and N–H). Deprotonation results in a further decrease of the NHO composition of N character in the P–N bonds, giving $sp^{1.1-1.5}$ hybridization.

The results presented in Table 2 reflect the opening of the P– N–P angle and its tendency to become linear, as shown by the NHO compositions of N character in P–N bonds. Therefore, in the case of ^{Me}LH, the small difference in the hybridization of N between the LH and L[–] forms, corresponds to a negligible change in the P–N–P angle upon deprotonation. On the other hand, the N hybridization in ^{Ph}LH is strongly reduced from sp^{1.7} to sp^{1.1} upon deprotonation, inducing the largest opening of the P–N–P angle. Ligands bearing ⁱPr peripheral groups lie in the middle between these two extreme cases.

 $\label{eq:Table 2} Table 2 \quad NHO \ composition \ of \ NBOs \ containing \ N \ character \ in \ the \ P-N \ bonds \ for \ the \ optimised \ structures \ of \ the \ LH \ and \ L^- \ forms$

(b) Origin of π delocalization and chemical bonding. NBO analysis of the spin-restricted B3LYP density matrix with respect to 6–311G* basis set, verifies that delocalization of π electronic density stems from distribution of the S and N LPs among both P atom p-orbitals.⁴⁰ The increase of π electronic density delocalization upon deprotonation is a direct consequence of the additional N LP. Depictions of these considerations are provided by the visualization of the proper NBOs and the corresponding NLMOs of N and S LPs. In the case of LH forms, both N and S LP NLMOs demonstrate π delocalization towards the P atoms, which is manifested as a distortion of the associated N and S LP NBOs (Fig. 2i,ii). This is also the case in the L⁻ forms. However, the existence of the additional N LP upon deprotonation enhances π delocalization, as is mirrored in the contour plot of the second N LP NLMO (Fig. 2iii).



Fig. 2 Selected NBOs (top) and the corresponding NLMOs (bottom) for LH (i,ii), and L^- (i, ii, iii) forms of the ligands. All contour plots were generated with NBOView 1.0 using a value of 0.03, and step size of 0.03.²⁶

The determination of NLMO/NPA bond orders also reflects the expected differences regarding P–S and P–N bonds, since the former are notably decreased and the latter are considerably increased upon deprotonation. For example, the NLMO/NPA bond orders calculated for the P–N bonds increase from approximately 0.5 in ^{Ph}LH to 0.626 in ^{Ph}L⁻, suggesting greater double bond character. On the contrary, the P–S bond orders diminish from approximately 1.21 to 1.104, indicating smaller double bond character after deprotonation (Table 3). These results are in excellent agreement

Table 3NLMO/NPA bond orders for the optimised structures of the
LH and L^- forms of the ligands

Ligand	NBO	Occupancy	N character (%)	N hybridization		-				
Met II	D2 N15	1.07705	79.2			NLMO/1	NPA bond o	rders		
^m LH	P3-N5	1.8//95	/8.3	sp.,	D 1	Max	Max	Der TT	iD: T	
	P4–N5	1.88883	78.6	sp ^{1.8}	Bond	^{Me} LH	^{wie} L ⁻	"'LH	$^{III}L^{-}$	
$^{Me}L^{-}$	P3–N5	1.98276	70.7	sp ^{1.7}						
	P4–N5	1.98634	71.4	sp ^{1.5}	P3–N5	0.509	0.678	0.496	0.631	
^{iPr} LH	P3–N5	1.98298	74.1	sp ^{1.8}	P4–N5	0.502	0.643	0.494	0.630	
	P4–N5	1.98297	74.2	sp ^{1.9}	P3-S1	1.263	1.107	1.213	1.074	
$^{iPr}L^{-}$	P3–N5	1.98263	72.3	sp ^{1.5}	P4–S2	1.253	1.107	1.204	1.078	
	P4–N5	1.98235	72.2	sp ^{1.5}						
${}^{\mathrm{i}\mathrm{Pr},\mathrm{Ph}}\mathrm{LH}$	P3–N5	1.98240	73.2	sp ^{1.9}		NLMO/1	NPA bond o	rders		
	P4-N5	1.98303	74.4	sp ^{1.8}						
$^{\mathrm{iPr,Ph}}\mathrm{L}^{-}$	P3–N5	1.98342	71.2	sp ^{1.5}	Bond	^{iPr,Ph} LH	$^{iPr,Ph}L^{-}$	^{Ph}LH	$^{\rm Ph}{ m L}^-$	
	P4–N5	1.98313	72.4	sp ^{1.4}						
Ph LH	P3–N5	1.98261	73.7	sp ^{1.7}	P3-N5	0.521	0.663	0.498	0.626	
	P4–N5	1.98253	73.6	sp ^{1.7}	P4–N5	0.485	0.613	0.507	0.626	
$^{\rm Ph}L^{-}$	P3–N5	1.98551	72.5	$sp^{1.1}$	P3-S1	1.223	1.103	1.216	1.104	
	P4-N5	1.98551	72.5	$sp^{1.1}$	P4–S2	1.223	1.109	1.211	1.104	

				¹ H chemical s	hifts/ppm				
	³¹ P chemica	l shifts/ppm		Ph groups			ⁱ Pr groups		
Compound	Ph ₂ P	ⁱ Pr ₂ P	$^{2}J(^{31}P-^{31}P)$	o-C ₆ H ₅	$m-C_6H_5$	$p-C_6H_5$	CH ₃	CH ₃	С–Н
1	-32.8			8.85 (16), br	6.58 (16), br	5.97 (8), br			
2		-331.9					10.62 (24), br	7.30 (24), br	1.45 (8), s
3	-87.8(1)	-188.4(1)		8.41 (8), d	4.75 (8), br	6.03 (4), d	9.45 (12), br	7.77 (12), d	1.49 (4), s
8	37.6								
9 ²⁹		64.4							
10 ³⁰	34.3	67.8	17.8 Hz						
$^{Ph}LH^{47}$	57.7								
^{iPr} LH ²⁹		91.3							
${}^{\mathrm{i}\mathrm{Pr},\mathrm{Ph}}LH^{30}$	51.5	100.0	30.8 Hz						

Table 5Selected IR data (cm^{-1}) for ligands and complexes 1–7

Compound	v(P–N–P)	v(PhP–E) ^a	v(ⁱ PrP–S)
PhLH ³⁴	935–925–920	648 (s)	_
^{iPr} LH ²⁹	933-904-878	_	646 (m)
^{iPr,Ph} LH ³⁰	935-907-880	624 (s)	613 (s)
$[Ph_2P(Se)]_2NH^{31}$	937-926-918	546 (s)	
132	1210 (br)	563 (s)	
2 ³²	1218 (br)	_	560 (s)
3	1231 (br)	573 (s)	527 (s)
4	1217 (br)	564 (s)	_
5	1223 (br)	_	549 (m)
6	1233 (br)	576 (s)	528 (s)
7	1205 (br)	536 (s)	
^{<i>a</i>} $E = S$ or Se.			

with the ³¹P NMR and IR spectroscopic data (Tables 4 and 5). Greater double bond character of the P–N bonds is reflected as an increase of v(PNP) in the IR spectra of the deprotonated ligands. Moreover, the electronic density on P atoms is increased, since P=N is less polarized than P=S, hence the ³¹P chemical shifts move to lower frequencies after deprotonation.

The geometrical and electronic changes upon deprotonation of LH described above, explain the flexibility of this family of ligands that enables them to be rather versatile in structural and metal-coordinating terms.^{11,12} Moreover, the DFT calculations presented so far, prove that the additional N LP and the necessity of the extra charge distribution that is generated upon deprotonation, is the dominant factor that imposes the structural changes observed by X-ray crystallography in these ligands.

Description of structures of ML₂ complexes

 $Co^{iPr,Ph}L_2$ (3). To the best of our knowledge, complex 3 is the second Co(II) complex with an asymmetric LH ligand, the first being the complex Co[Ph₂P(S)NP(S)Me₂]₂.⁴² Selected bond lengths and angles of complex 3 are listed in Table S1[†] and the ORTEP representation of its crystal structure is presented in Fig. 3.

The complex has crystallographically-imposed twofold symmetry and the CoS_4 core exists in a distorted tetrahedral form, as depicted from the magnitude of S–Co–S angles, which range between 95.84(2)° and 114.225(13)°, the S…S non bonding distances ranging between 3.467 Å and 3.898 Å, as well as the dihedral angles between the CoS_2 pairs being 87.2°, 81.3° and 83.9°. Moreover, the Co–S bond lengths are not equivalent to each



Fig. 3 Molecular structure and atom numbering of complex 3 (ORTEP diagram, 50% thermal ellipsoids). Atoms with labels ending in "_2" are at equivalent positions (-x,y,1/2 - z).

other, ranging between 2.3061(4)Å and 2.3356(4) Å, possibly due to different R groups (Ph or ⁱPr) attached to the P atoms. However, this is not the case for the analogous $Co[Ph_2P(S)NP(S)Me_2]_2$ complex, in which the Co–S bond lengths are all equivalent to each other.⁴²

As expected, the P-N-P angles are increased compared to ${}^{iPr,Ph}LH$, from 129.5(3)° in the latter, to 139.21(8)° in 3, whereas in the case of the Co^{Ph,Me}L₂, P-N-P angles are barely affected, compared to Ph,MeLH.42 This observation provides experimental evidence concerning the effect of the iPr groups on the enlargement of the P-N-P angle. The same phenomenon has also been observed in the case of the ^{iPr}LH ligand and the pseudo-tetrahedral complexes it forms with Mn(II) (5), as well as Co(II),³² Cd(II) and Zn(II) ions.²⁹ In these complexes, the P-N-P angles vary between 137° and 143°. Presence of the Pr bulky groups seems to be responsible for the opening of the P-N-P angle which does not take place when the ligand possesses other R groups such as Me³⁷ or OPh.⁴³ Even in complexes 1^{32} and 4^{33} bearing $^{Ph}L^{-}$, the P-N-P angle does not change, compared to PhLH. Therefore, although deprotonation enhances the P-N-P angle enlargement, as discussed above, steric effects imposed by the peripheral groups seem to regulate the magnitude of the P-N-P angle in the ML_2 complexes.

The P–S and P–N bond lengths in complex **3** are 2.0194(5) Å and 2.0361(5) Å, and 1.5826(12) Å and 1.5915(12) Å, respectively, having, as expected, intermediate magnitudes between single and double bonds, compared to ^{iPt,Ph}LH.³⁰

The CoSPNPS ring in complex 3 adopts a pseudo-boat conformation, but in contrast to all other known Co(II) complexes with this type of ligands, Co and N are the "bow" and the "stern" of the boat instead of P and S (Fig. S1[†]). This should be the case for all tetrahedral complexes involving Ph,iPrLH, as it was also observed for the corresponding Mn(II) complex 6. The Co-S-P angles are of the same order as those in complex 6, at $98.553(18)^{\circ}$ and 101.835(18)°. These angles are considered to be in the expected range for M-S-P angles in a six-membered pseudo-boat ring, with M (M = Co, Mn) and N atoms at the apices. This leads to an axial-equatorial interaction between Ph and Pr groups attached to different P atoms on the same chelate ring (Fig. S1[†]). However, the axial and equatorial positions are also distorted due to the very specific boat ring geometry. Complexes 3 and $Co^{Ph,Me}L_2$ provide a rare example of different MSPNPS metallacycle conformations upon variation of the peripheral R groups. Co^{Ph,Me}L₂ adopts a chair conformation and consequently the interactions between the corresponding peripheral groups in the same chelate ring are axialaxial, implying relaxation of the chelate ring due to the presence of Me groups⁴² (Fig. S2[†]).

 $Mn^{Pr}L_2$ (5). Selected bond lengths and angles of complex 5 are listed in Table S1[†]. The representation of the ORTEP plot of its molecular structure is presented in Fig. 4.



Fig. 4 Molecular structure and atom numbering of complex 5 (ORTEP diagram, 50% thermal ellipsoids).

The Mn–S bond lengths are typical of Mn–S unstrained bonds. It should be noted that, as in the case of complex **3**, the Mn–S bond lengths are not equivalent. The compound can be described as a spiro-bicyclic structure with Mn being the spiro-atom. The MnS₄ core adopts a slightly distorted tetrahedral geometry, as it can be reflected by the magnitude of the S–Mn–S angles, which lie between 107.35(2)° and 111.53(2)°. The endocyclic bite angles S(1)–Mn–S(2) and S(3)–Mn–S(4) are 109.59(2)° and 110.82(2)°, respectively, with the former being nearly the angle of an ideal tetrahedral geometry. Planes defined by the endocyclic S–Mn–S angles are nearly perpendicular to one another (angle between planes is 88.10°). Therefore, the molecule is very close to having an ideal tetrahedral geometry. It is only the slight deviation from the angle of an ideal tetrahedron, as well as the asymmetric bond lengths, that break this symmetry.

The average P–S (2.028 Å) and P–N (1.592 Å) bond lengths are enlarged and shortened, respectively, compared to the free ligand $^{iPr}LH.^{29}$ In the latter, the P–S bond lengths are 1.941(1) Å and 1.949(1) Å, whereas the P–N ones are 1.682(3) Å and 1.684(2) Å. Therefore, the P–S and P–N bonds in complex 5 are between The MnSPNPS ring adopts a pseudo-boat conformation, with the P and S atoms at the apices, being the "bow" and the "stern" of the boat respectively, in agreement with other metal complexes of similar ligands^{12b} (Fig. S3).† The Mn–S–P angles, ranging between 104.75(3)° and 105.60(3)°, are the expected ones for a boat conformation with P and S at the apices. In this conformation, the interactions between the ¹Pr groups on different P atoms of the same chelate ring are axial–equatorial, thus affording a more stable conformation compared to a pseudo-chair one.³³

 $Mn^{iPr,Pb}L_2$ (6). Complex 6 was crystallized in space group *P*1, with one molecule per unit cell. Space group *P*1 is rather unusual for crystal structures of non-enantiopure materials. Selected bond lengths and angles of complex 6 are listed in Table S1[†] and the ORTEP representation of its molecular structure is presented in Fig. 5.



Fig. 5 Molecular structure and atom numbering of complex 6 (ORTEP diagram, 50% thermal ellipsoids).

The Mn–S bond lengths are again typical of unstrained Mn–S bonds, ranging between 2.4348(10) Å and 2.4578(10) Å, although they are crystallographically non-equivalent to each other. The MnS₄ core adopts a distorted tetrahedral geometry, as can be deduced from the S–Mn–S angles that range between 96.91(3)° and 117.01(4)°, as well as the value (78.99(3)°) of the angle between S(1)–Mn–S(2) and S(3)–Mn–S(4) planes. The P–N–P angles are increased, compared to ^{iPr,Ph}LH,³⁰ from 129.5(3)° in the latter, to 141.2(2)° and 140.8(2)° in complex **6**.

It is of interest to note that the apices of the pseudo-boat conformation of the metallacycle are occupied by Mn and N (Fig. S1),† instead of the expected S and P atoms. This fact is rather unusual for this type of complex in tetrahedral geometry, as it has up to now been observed only in complex **3** and in $Fe^{Me}L_2$.⁴⁴ It should be pointed out that the interactions between the ¹Pr and Ph groups on different P atoms in the same chelate ring are again axial–equatorial, although the axial and the equatorial positions are now distorted due to a different boat conformation (Fig. S1).†

 $Mn[Ph_2P(Se)NP(Se)Ph_2)]_2$ (7). Selected bond lengths and angles of complex 7 are listed in Table S1[†] and the ORTEP representation of its molecular structure is presented in Fig. 6. Complex 7 was synthesized in order to assess the structural and spectroscopic changes induced by replacing S by Se in complex 4.



Fig. 6 Molecular structure and atom numbering of complex 7 (ORTEP diagram, 50% thermal ellipsoids).

The Mn-Se bond lengths vary between 2.5344(11) Å and 2.5691(11) Å, but they are slightly longer compared to typical Mn-S bonds in the complexes 4-6, due to the larger radius of the Se atom compared to the S atom. This spiro-bicyclic Mn(II)Se₄ compound adopts a slightly distorted tetrahedral conformation, with the Se-Mn-Se angles varying between 102.90(4)° and $113.75(4)^{\circ}$. The Se · · · Se non bonding distances range between 4.276 Å and 4.264 Å, and the dihedral angles between MnSe₂ pairs are 87.41°, 87.01°, and 84.37°. As described extensively above, the P–N–P angles are slightly increased compared to the corresponding LH form, being 132.2(3), 136.3(3) in complex 7 and 132.3(2)° in LH.³¹ The MnSePNPSe ring adopts the usual pseudo-boat conformation with the P and Se atoms at the apices. As is expected, due to this chelate ring geometry, the interaction between the Ph groups on different P atoms on the same chelate ring is axial-equatorial (Fig. S3).[†]

Electronic spectroscopy

An ideal tetrahedral d⁷ ion is expected to show transitions from the ground ${}^{4}A_{2}$ state to the excited ${}^{4}T_{2}$ (v₁), ${}^{4}T_{1}(F)$ (v₂) and ${}^{4}T_{1}(P)$ (v₃) states.⁴⁵ The electronic spectrum of **3** (0.5 mM in CH_2Cl_2) showed ligand-field bands at 16181 cm⁻¹, 14144 cm⁻¹, 13 123 cm⁻¹ (shoulder) and 6630 cm⁻¹, consistent with Co(II) d-d transitions that are typical of a tetrahedral Co(II)S₄ coordination environment. The band at 16181 cm⁻¹ is believed to arise from a formally forbidden transition to a doublet state,^{45a} the transitions at 14144 and 13123 cm⁻¹ to v_3 , and the broad unresolved band centred at 6630 cm⁻¹ to v_2 . The v_1 transition is expected to be in the IR region (ca. 3000 cm⁻¹) and thus it is not observed. Splittings within the observed bands may arise due to distortion from ideal symmetry or spin-orbit coupling.^{46b} A further band was observed at 32154 cm⁻¹ with a shoulder at 27100 cm⁻¹, assigned as S \rightarrow Co(II) charge transfer. From the ligand-field bands, the values of $\Delta_t = 3980 \text{ cm}^{-1}$ and $B' = 660 \text{ cm}^{-1}$ can be derived using the Tanabe-Sugano diagram. There is some uncertainty in this determination due to the difficulty in assigning the centre of the broad bands

observed. However, these values are consistent with those observed for complex 1,³⁴ and show the L⁻ forms to be strong-field ligands. The nephelauxetic parameter ($\beta = B'/B_{\text{free ion}}$) is calculated as 0.68 (since *B* for the free Co(II) ion is 971 cm⁻¹), indicating a significant degree of covalency for such Co(II)S₄ systems.^{8a,45,46}

NMR spectroscopy

To the best of our knowledge, the ¹H NMR spectrum of complexes 1 and 2 have not been reported up to now. The ¹H NMR spectrum of 1 at 298 K reveals broad signals for each set of aromatic protons, *i.e.* $\delta = 8.85$ ppm (*ortho*), 6.58 ppm (*meta*) and 5.97 ppm (*para*). Similar behaviour has been reported for tetrahedral paramagnetic Ni(II) complexes bearing PhL-.47 On the other hand, this is not the case for the diamagnetic complex $Zn^{Ph}L_2$ (8), where the ortho and para aromatic proton resonances are not separated. In the case of complex 2, the presence of the paramagnetic Co(II) center (S = 3/2) strongly affects, as expected, the chemical shifts of the ⁱPr peripheral groups. The methyl groups become magnetically inequivalent and extremely deshielded, giving rise to two broad signals at 10.62 ppm and 7.30 ppm, respectively, while the C-H proton is observed at 1.45 ppm. Complex 3 shows a very complicated ¹H NMR spectrum, illustrating again the effect of unpaired electrons of Co(II) on the chemical shifts.

Proton-decoupled ³¹P NMR spectra of complexes **1–3** were recorded at 298 K in CDCl₃. Table 4 incorporates both previously published³² and new data from this work. The dramatic reduction in the ³¹P chemical shifts compared to the corresponding deprotonated ligands can be attributed to the paramagnetic Co(II) center. On the other hand, the large difference in chemical shifts between **1** and **2** (–32.8 ppm and –331.9 ppm, respectively) cannot solely be explained by the electron-donating effect of the ⁱPr groups. It is worth noticing that a single peak at –150.0 ppm was reported for complex **2**,³² whereas a peak at –331.9 ppm was observed in this work. The latter was double-checked by monitoring the spectrum also at 500 MHz (Bruker), and therefore, we believe that the value quoted in ref. 32 must be erroneous.

Furthermore, this immensely up-field shifted new resonance for complex 2, discloses the fact that complex 3, bearing the asymmetrical ^{iPr,Ph}L⁻ ligand, exhibits intermediate chemical shifts compared to complexes 1 and 2. The ³¹P NMR spectrum of complex 3 reveals two signals for the non-equivalent P atoms, without any well resolved hyperfine couplings, at -87.8 ppm for PPh₂ and at -188.4 ppm for PⁱPr₂. In other words, PPh₂ is shielded, while PⁱPr₂ is deshielded compared to 1 and 2 which contain the symmetrical ligands ^{Ph}L⁻ and ^{iPr}L⁻, respectively. We propose that this trend is explained *via* an electron density flow from the PⁱPr₂ fragment carrying the electron withdrawing Ph groups, *via* the central metal atom.

This trend has not been previously considered, although it seems to also appear, to a less significant extent, in the thoroughly studied protonated forms of the ligands (Table 4), due to their delocalized π electronic density. However, the presence of a central metal ion with unpaired electrons is clearly promoting, if not altering, this electron density flow, since, apart from the Co(II) complexes discussed here, similar behaviour is documented in the corresponding series of tetrahedral paramagnetic complexes with Ni(II) (S = 1), as will be reported elsewhere. The participation of paramagnetic metal ions in this electronic channel is further supported by the comparison of the ³¹P NMR spectra of the respective series of Zn(II) complexes 8 (this work), Zn^{iPr}L₂ (9)²⁹ and Zn^{iPr,Ph}L₂ (10),³⁰ in which the same trend is observed, albeit with minor differences in ³¹P chemical shifts that resemble those of the free ligands (Table 4). The diamagnetic nature of Zn(II) seems to allow electron density flow only among the chelate rings.

The above results can be considered as evidence of extensive delocalization of electronic density from the Co(II) center onto the ligands in complexes 1–3, due to the presence of highly covalent Co(II)–S bonds.

IR spectroscopy

The IR spectrum of complexes synthesized in this work exhibit the expected and well documented trends, regarding the P–N and P–S bond orders.^{29,31,39} The P–N bonds are strengthened, while the P–S(Se) bonds are weakened, as can be deduced from the comparison of the v(PNP) and v(PS) or v(PSe) between the metal complexes and the free ligands (Table 5). Higher energies of the v(PNP), correspond, not only to stronger P–N bonds, but to larger values of PNP angles, as well (Table S1).†

EPR spectroscopy

MnL₂ complexes. Room temperature EPR studies of complexes 4, 5, 6 and 7 showed a characteristic six-line pattern arising from coupling to the I = 5/2 Mn nucleus. Frozen glass EPR studies of 4–7 show a signal of 16 lines comprising 6 main peaks with 5 sets of doublets due to spin forbidden transitions (Fig. 7, Table 6). This pattern is characteristic of Mn(II) in a tetrahedral site with an isotropic g parameter, consistent with the nearly perfect tetrahedral geometry observed in the solid state for 4–7.⁴⁸ The



Fig. 7 Frozen glass EPR spectrum of complex 5 at 9.48 GHz and 77 K.

similarity of the EPR parameters in solution would suggest that the complexes do not differ greatly in geometry when in solution. Therefore, for the series of the MnL_2 complexes, it seems likely that the deviations in their geometry in the solid state reflect packing effects rather than electronic properties of the ligands.

The hyperfine coupling constant A_1 for $[MnCl_4]^{2-}$ is 79.3 G and the value of A_1 has previously been taken as evidence of the level of covalency in the Mn–ligand bonding.^{48c,d} The significantly larger values of A for 4–7 in comparison with $[MnCl_4]^{2-}$ (Table 6) are consistent with location of the spin density on 4–7 mainly on the metal centre and not the ligands and thus a low component of covalent bonding in the metal–ligand interaction. Interestingly, 7 appears to be the least covalent of the complexes with a distinctly larger value of A than the sulfur-donor complexes 4–6.

CoL₂ complexes. The CoL₂ complexes 1, 2 and 3 studied in this work are EPR silent in the X-band at temperatures as low as 77 K. We attempted to record spectra at room temperature (in solution and as powders) and also frozen at liquid nitrogen temperature, however, these were all silent. EPR silent Co(II) species have been observed before, and the effect was attributed to rapid spin relaxation through spin–lattice interactions.⁴⁹

Magnetic susceptibility studies

Magnetisation *versus* temperature was recorded for complexes 1–7 at temperatures ranging from 2 K to 340 K, at 0.1 T and the molar magnetic susceptibilities, corrected for a diamagnetic contribution, were plotted against temperature (Fig. 8). Data for 1–7 could all be fit in the high-temperature region to the Curie–Weiss model with Curie constants of C = 1.89 (1), C = 2.17 (2), C = 1.85 (3), C = 4.42 (4), C = 4.25 (5), C = 4.56 (6) and C = 4.73 (7)



Fig. 8 A plot of the square of the effective magnetic moment of **3** against temperature showing a sharp drop at low temperature due to zero-field splitting of the ground state. The solid line is a fit to the model in ref. 51 and yields a zero-field splitting parameter of 24 K.

Table 6	EPR parameters for complexes 4–7 compared to $MnCl_4^{2-}$
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Complex	g	A_1/G (main line splitting, average)	A_2/G (Doublet splitting, average)
4 5 6 7 [MpC].1 ^{2-48c}	2.06 2.07 2.01 2.01 2.01	89.5 93.7 90.9 97 79.3	22.1 23.4 25.2 31

emu K mol⁻¹. Complexes **1–7** show a negligible Weiss constant, indicating no significant intermolecular interactions. This is to be expected as the X-ray crystal structures show only limited short contacts between the peripheral groups (Ph or ⁱPr), which do not mediate spin interactions efficiently. Thus, the peripheral groups effectively shield the metal centers from intermolecular interactions, since the $M \cdots M$ distances between molecules are large (of the order of 10 Å). Therefore, complexes **1–7** behave like nearly perfect paramagnetic systems.

High spin Co(II) and Mn(II) have 3 and 5 unpaired electrons, respectively, and no first order spin–orbit contribution, giving a theoretical spin-only Curie constant of 1.875, and 4.377 emu K mol⁻¹ respectively, which is in close agreement with the experimental results. For the Mn(II) complexes, the *g*-values are within errors consistent with those determined by EPR (see above).

Literature examples of tetrahedral Co(II) complexes typically have higher Curie constants, in the region of 2.6, due to mixing in of low-lying excited states.⁵⁰ In the case of **2**, this may account for the higher value of *C* as this complex is the closest to a tetrahedral geometry, whereas **1** and **3** show larger distortions that will split the three-fold degeneracy of the first excited state and so mixing-in of an orbital component to the magnetic moment will be much reduced. This leads to values closer to the spin-only value.

The data for complexes 1 and 3 were fit over the entire temperature range using an expression that accounts for the observed zero-field splitting of the ground state which results in a drop in effective magnetic moment at low temperature.⁵¹ From these fits, values of the zero-field splitting parameter of J/kB = 20 K and 24 K were obtained for 1 and 3, respectively. These values are largely comparable to literature data but are slightly larger than typical values⁵¹ possibly arising from the strength of the L⁻ ligand field. A comparable fit for complex 2 was not possible, due to more complex magnetic behaviour at lower temperature, and no further analysis was attempted in the absence of low-temperature structural data.

We sought to fit the data for complexes 1 and 3 using eqn (1), which is appropriate for the powder susceptibility of an axially distorted Co(II) four coordinate system and this should apply exactly to our complexes.⁵² Using a range of reasonable values for the parameters *e.g.* (in cm⁻¹) $\Delta_1 = 3300$, $\Delta_2 = 3700$, δ (zerofield splitting) = 10, $\lambda = -160$, we could successfully reproduce the data for the complexes. However, we were not able to obtain an optimised fit, since there are too many parameters to be determined from the relatively simple curve. Thus, the data are consistent with this model but we cannot use the data to extract the resulting parameters. To fit the parameters additional data would be required, such as oriented single crystal magnetic data, however, the crystals available were not sufficiently large to enable this type of experiment.

$$\chi = (N\beta^2/3kT)[5y^2 + 10x^2 + (2\delta/kT)(y^2 - x^2)] + \text{TIP}$$
(1)
$$x = 1 - (4k\lambda/\Delta_2)$$
$$y = 1 - (4k\lambda/\Delta_1)$$

Eqn (1): N = Avogadro's number, $\beta = \text{the Bohr magneton}$, k = Bohr magneton, $\delta = \text{zero-field splitting of the ground } {}^4\text{B}_1$ state, $\Delta_1 = \text{splitting between ground } {}^4\text{B}_1$ state and ${}^4\text{B}_2$ state and $\Delta_2 = \text{splitting between ground } {}^4\text{B}_1$ state and ${}^4\text{E}$ state. Temperatureindependent paramagnetism (TIP) is estimated according to TIP = $8N\beta^2/\Delta$ using an averaged value of Δ).

Covalency of the M(II)-S bonds from experimental data

MnL₂ complexes. The Mn(II)–S bonds in the MnL₂ complexes studied in this work, appear to have a relatively low covalent character, since spin density is maily located on the central metal ion Mn(II), as is deduced from the EPR data. The Mn–Se bonds in complex 7 seem to be slightly less covalent compared to the Mn–S bonds. This might be due to the smaller electronegativity of Se compared to S, or to less well matched orbital energies for the Mn–Se compared to the Mn–S bonding interaction.

CoL₂ complexes. The nephelauxetic ratio β has been used in the past as an indicator of covalency for Co(II)–S containing complexes, with values ranging between 0.6 and 0.7.⁴⁶ The value of 0.68 that was obtained for complex **3** in this work, is well within these limits and proves that the Co(II)–S bonds in this complex have considerable covalent character.

The value of the spin–orbit coupling parameter λ is considered as another indicator of covalency. Values of λ within 60 to 90% of the free ion value (-178 cm⁻¹) have been obtained for a series of tetrahedral [Co(II)X₄]^{2–} complexes, in which the β values range between 0.65 to 0.80.⁵³

A third indicator of covalency, is the value of the orbital reduction parameter k, which for Co(II)S₄ complexes was determined to be smaller compared to other Co(II) complexes.⁵¹ More specifically, for Co(II)S₄ chromophores, values of k are 0.7,⁵¹ for a CoN₄ chromophore 0.8,⁵⁴ for Co(II)O₄ 0.9,⁵⁵ and for [CoCl₄]^{2–} 0.92.⁵⁶ These data were considered as indicative of more extensive covalency of Co(II)–S bonds compared to the other cases.

Theoretical calculations on the ML_2 complexes (M = Mn, Co)

The complexes $Co^{Me}L_2$ (11) and $Mn^{Me}L_2$ (12) were chosen as models, in order to investigate the electronic properties of the ML_2 (M = Co, Mn) complexes. Complex 11 has already been synthesized and structurally characterized by X-ray crystallography, but the crystallographic coordinates are not available in the Crystallographic Database. By comparing the published crystallographic coordinates³⁷ to the previously crystallized complex 1,³² we found similarities that led us to build a theoretical model of 11 from the crystal structure of 1. The same procedure was applied for the as yet unknown complex 12, by using the previously published structure of complex 4.³³ Complexes 11 and 12 are expected to be paramagnetic with 3 and 5 unpaired electrons, respectively.

For complexes **11** and **12**, the Density Functional wavefunctions (*i.e.* the Kohn Sham orbitals) were calculated in two ways: first, a spin-restricted calculation (ROB3LYP, $\langle S^2 \rangle = 3.75$ and $\langle S^2 \rangle =$ 8.75) was carried out as the simplest description of an open shell system.⁵⁷ In this case, the total spin density is reflected in either the HOMO or the LUMO wave functions (Singly Occupied MOs, SOMOs), since all other orbitals are either doubly occupied or doubly unoccupied. However, since the spin polarization effect is important, spin-unrestricted calculations (UB3LYP, $\langle S^2 \rangle \approx 3.75$, and $\langle S^2 \rangle \approx 8.75$) were also performed.⁵⁷ Single point calculations by using the TZVP basis set for all atoms, on the ground state calculated geometries, were then performed for the visualization of the frontier MOs and the NBO analysis. In order to describe

$[(SPMe_2)_2]$	$[(SPMe_2)_2]N^-$		11		12	
Bond	Bond Order	Bond	Bond Order	Bond	Bond Order	
av P–N	0.67	av. P–N	0.71	av.P–N	0.70	
av P–S	1.09	av. P–S	0.97	av.P–S	0.96	
		av. Co–S	0.22	av. Mn–S	0.18	

Table 7 Selected NLMO/NPA bond orders for MeL, 11 and 12 in TZVP basis set

the bonding between the metal and the ligands, the ML⁺ and L⁻ molecular fragments were chosen for the charge decomposition analysis, as well as the MO composition of the whole molecules in terms of molecular fragments.⁵⁸

Properties of the M-S bonds

The comparison between the NBOs, in complexes **11** and **12**, describing free and coordinated ${}^{Me}L^-$ ligands indicates that P–S and P–N bonds are only slightly further weakened and strengthened, respectively, due to complexation. The P–N–P angles in **11** and **12** are very similar to those of ${}^{Me}L^-$, again implying that in the absence of steric interactions between R peripheral groups, P–N–P angles in tetrahedral ML₂ complexes are mainly affected by the deprotonation and not by the complexation of the ligands (Tables 7 and 8).

In ML₂ complexes, ^{Me}L⁻ lies at higher energy than the previously calculated free ^{Me}L⁻, by 6.75 Kcal mol⁻¹ (M = Co) and 7.83 Kcal mol⁻¹ (M = Mn), with respect to the TZVP basis set. In other words, it seems that ligands of this family become energetically poised to coordinate to metal ions.

The Co–S bond in **11** is shorter than the Mn–S bond in **12**. As it has been reported previously,⁵⁸ shorter bond lengths usually correspond to higher bond orders, although variations have been observed. Various types of bond order evaluations (NLMO/NPA, Meyers, Wiberg, Lowdin) support this hypothesis (Table 7). The Co–S bond order is greater than the Mn–S one (Table 7); therefore,

Table 8Selected structural properties from the crystal structures (exp)and the optimized geometries (calc) of $M^{Me}L_2$ complexes

	11		1	12	4
Bond	Calc	Exp	Exp	Calc	Exp
av. M–S (Å)	2.376	2.314	2.329	2.481	2.443
av. P–S (Å)	2.065	2.021	2.011	2.064	2.013
av. P–N (Å)	1.613	1.586	1.588	1.610	1.588
av. S-M-S $_{endo}$ (°)	109.4	109.8	113.9	108.1	111.8
av. M–S–P (°)	102.6	102.4	100.3	102.5	99.8
av. S–P–N (°)	117.2	116.9	118.3	118.1	118.7
av. P–N–P (°)	128.7	128.9	129.5	131.6	133.2

Table 9 NPA charges and MPA/NPA spin densities for 11 and 12

both bond lengths (Table 8) and bond orders suggest that the covalent contribution in the M–S bonds in $Co^{Me}L_2$ is higher compared to $Mn^{Me}L_2$.

The chemical bonding in transition metal complexes is usually described in terms of covalent and ionic interactions between the metal centers and the ligands:

(i) Ionic character of the M-S bonds

It has been shown⁵⁸ that for an M–S(thiolate) bond, the ionic character is mirrored in the absolute values of the atomic charges of the M and S atoms, as higher values correspond to higher ionic character. The M–S bonds in **12** presents a higher degree of ionicity compared to **11**, as can be derived from the NPA population analysis (Table 9).

(ii) Covalent character of the M-S Bonds

The covalent interaction between two molecular fragments is usually described in terms of electron donation. Molecular orbitals HOMO-0 (Sp_o*), -1 (Sp_π*), -2 (Sp_π), -3 (Sp_o), -5(Lp_o) of the ^{Me}L⁻ molecular fragment (Fig. 9) participate in M–S bonds. It should be pointed out that electron density is centered on S atoms in the first four MOs, while in HOMO-5 electron density is distributed among SPNPS rings.



Fig. 9 Frontier MOs of the MeL- molecular fragment.

The metal centers in **11** and **12** typically contain M^{2+} ions. However, calculated NPA partial charges are lower than +2 (Table 9), suggesting ligand to metal electron donation and thus revealing the covalent character of the M–S bonds. Calculation of the Mulliken and Natural Magnetic spin densities of the metal ions and the sulfur atoms, also reveals that part of the electron

11			12			
Atom	NPA charges	MPA/NPA spin densities	Atom	NPA charges	MPA/NPA spin densities	
Со	+1.08	2.521/2.501	Mn	+1.26	4.769/4.438	
S_1	-0.70	0.105/0.113	S_5	-0.74	0.036/0.110	
S ₂	-0.70	0.105/0.113	S ₇	-0.74	0.037/0.110	
$\overline{S_3}$	-0.70	0.106/0.113	S_8	-0.74	0.037/0.110	
S_4	-0.70	0.106/0.113	\mathbf{S}_{9}	-0.74	0.037/0.110	

Table 10	Total contributions of unoccupied fragment molecular orbitals
to the occ	upied orbitals of complexes 11 and 12

	11	12					
Donation $(L \rightarrow ML^{-})$ and Polarization	tion of ML+						
% (α-spin UFO of ML ⁺) % (β-spin UFO of ML ⁺)	21.0 142.9	23.1 36.9					
Donation (ML ⁺ \rightarrow L) and Polarizati	Donation (ML ⁺ \rightarrow L) and Polarization of L						
% (a-spin UFO of L) % (β -spin UFO of L) a-spin L \rightarrow ML ⁺ charge donation β -spin L \rightarrow ML ⁺ charge donation	6.1 6.6 0.19 e 0.37 e	5.8 4.2 0.14 e 0.30 e					

density is transferred from the central metal atom to the sulfur atoms (Table 9).

The covalent character of the M–S bond can be depicted by the interaction of the ML⁺ and L⁻ fragment orbitals. Ligand to metal electron donation can be considered as the mixing of the unoccupied MOs of the ML⁺ fragment with the occupied MOs of the L⁻ fragment. The Charge Decomposition Analysis reveals that the metal–ligand covalent interraction is dominant, involving charge donation from the L⁻ fragment to the ML⁺ one (Table 10). On the contrary, back donation is negligible.⁵⁸

The discussion on the ineraction diagrams of the molecular fragments will be focused on the β frontier MOs of the fragments

(Fig. 10), since the α MOs are occupied in both Mn(II) and Co(II), and thus contribute equally to the covalent character of the M– S bonds in both cases. The α spin LUMO of the ML⁺ fragment (64–65% in M 4s character) is mixed with the HOMO-2 (Sp_{π}) and the HOMO-3(Sp_{σ}) of the L⁻ fragment (Fig. S4).† This results in a small and relatively similar covalent interaction between the two fragments for both **11** and **12**. This is also reflected in the contribution of the α -spin ML⁺ unoccupied fragment molecular orbitals to the occupied orbitals of the complexes as a whole (Table 10).

In the case of 12, the β LUMOs 0, 1, 2, 3, 4 of the MnL⁺ fragment derive from the 3d metal orbitals (Fig. S5),† as it is supported by MPA. Since the Z_{eff} of Mn²⁺ is large, the difference in energy between the thiolate-based HOMOs of L⁻ and metal-based LUMOs of MnL⁺ is also large. As a consequence, a weak MO interaction is observed, producing a quite high HOMO-LUMO gap (4.6 eV). Contribution of the 3d orbitals in the occupied MOs of 12 corresponds to values smaller than 4%, revealing negligible interaction with the ligand MOs, and thus a minor covalent contribution.⁵⁸

The covalent character in the Mn–S bond emanates from mixing of the LUMO (30% in Mn 4s character) of the MnL⁺ fragment with the HOMOs of the L⁻ fragment (Fig S5†).⁵⁸ This additional interaction causes a further ligand to metal charge donation and the contribution of the β -spin MnL⁺ unoccupied fragment molecular orbitals to the occupied MOs of complex **12** increases to 36.9% (Table 10).



Fig. 10 β -spin energetic levels of the frontier MOs of complexes 11 and 12.

On the contrary, in the case of 11, metal orbitals d_{z2} and d_{yz} that were unoccupied in 12, become occupied are stabilized in the HOMO manifold. The sulfur character in the metal based LUMOs increases to ~19% while 3d metal character in the ligand based HOMOs Sp_π and Sp_σ increases to 8% and 3%, respectively (Fig. 10). Thus fragment mixing is enhanced and the energy of the LUMO manifold is lowered, resulting in a smaller HOMO-LUMO gap (3.6 eV).

It is noteworthy that HOMO-12 originates from $3d_{yz}$ of Co(II) and Sp_{σ} and Lp_{σ} of the ligand (Fig. 10, S6†), showing clearly the σ covalent character of the Co–S bond. It should be remembered that in the case of **12**, the β spin LUMOs (Mn 3d character) do not participate in any interactions, thus elucidating the lower covalent character of the Mn–S bond compared to the Co–S one, as well as the smaller ligand to metal charge transfer for complex **12** (Table 10).

Additional information on the estimation of the M–S covalency can be obtained by determining the number of the metal–ligand shared electrons (Table 11).²⁵ The covalency in the M–S bond has σ character, as can be seen by the corresponding NBOs in Fig. 11. In agreement with the experimental data described above, the covalency in the Co–S bond estimated by theoretical calculations is found to be larger compared to the Mn–S bond. The extent of covalency in the Mn–S and Co–S bonds, arising from π ligand to metal electron donations is reflected in the picture of the S LP NBOs and the corresponding NLMOs for the CoL₂ and MnL₂ complexes, respectively (Fig. 11).

Covalency of M-S bonds in biological systems

Compared to the above estimation of covalency in M-S containing sites by experiment and theory, a more direct experimental method, that of S K-edge X-ray absorption, has recently been developed by Solomon and colleagues, and applied to a series of inorganic and bioinorganic systems.15,59 According to this analysis, the intensity of the pre-edge peaks in the XAS spectrum are direct indicators of M-S covalency. Rather strong covalency is established in the case of Cu(II)-S and Ni(II)-S complexes. On the other hand, Co(II)-S is considered as a typically covalent bond, whereas the Mn(II)-S bond is shown to lack any considerable covalent character.^{59a} Preliminary results by SK-edge XAS studies on the covalency of Mn(II), Co(II), and Ni(II) complexes with the ligands used in the present study, are in agreement with the above observations, (P. Kyritsis, E. I. Solomon et al., unpublished). XAS S K-edge studies have also been carried out on many metalloenzymes containing M-S bonds.15,59 Functional consequences of the covalency of M-S bonds have been proposed for the Cu(II)-S(Cys) bond as the exit point in the electron transfer mechanism



Fig. 11 (A) Co–S and Mn–S bonding interactions within the NBO basis, showing the σ covalent character of the M–S bonds. (B) NBOs (up) and the corresponding NLMOs (bottom), showing the extence of covalency in the M–S bonds due to π ligand to metal donation. All contour plots were generated with NBOView 1.0 using a value of 0.03, and step size of 0.03.²⁶

of plastocyanin, ascorbate oxidase and nitrite reductase, as well as the di-copper and S(Cys)-bridged site of cytochrome oxidase. In the latter case, the extensive delocalization of electronic density is thought to result in lower reorganization energy, facilitating electron-transfer by this site. Moreover, the covalent nature of Fe–S bonds is manifested in the electronic and redox properties of Fe/S-containing rubredoxins and ferredoxins.^{15,59} Numerous other metalloenzymes have been shown to contain covalent M– S bonds that control the electronic properties of their active site needed for specific catalytic functions. Representative examples include the Fe-containing enzymes nitrile hydratase,²⁵ and superoxide reductase,⁶⁰ as well as the Ni superoxide dismutase.⁶¹

On the other hand, although covalency has been observed in various Co(II)–S complexes, to the best of our knoweledge, there has been no XAS or any other study of the covalency of Co–S in the active site of Co–S containing enzymes or "maquettes". The work presented here supports previous studies on Co(II)–S containing complexes, showing that the Co(II)–S bonds are typically covalent, in a large variety of coordination spheres. It would be expected that similar effects operate in the active sites of the Co(II) enzymes, and it would be interesting to study covalency aspects of Co(II)–S bonds in the active sites of these enzymes.

 Table 11
 Calculated M-L bond covalencies in terms of shared electrons for complexes 11 and 12. Bond covalencies were calculated with respect to the 6-311 G* basis set

11			12		
Bond	Bond covalency	Total covalency	Bond	Bond covalency	Total covalency
Co–S ₁	0.401 e ⁻	1.624 e ⁻	Mn–S5	0.376 e ⁻	1.463 e-
$Co-S_2$ $Co-S_3$	0.394 e ⁻ 0.408 e ⁻		$Mn-S_7$ $Mn-S_8$	0.358 e ⁻ 0.374 e ⁻	
Co–S ₄	0.421 e ⁻		Mn-S ₉	0.355 e ⁻	

II.⁹ How its sensin there ha is coord attempts Mn tran The lack in terms pronoun is of inte (comparseries 4– The la utilized to O chemis site in ru (high-spi between bonds in

The situation with respect to Mn(II)–S bonds in biology is completely different. Mn is found in many enzymes, the most characteristic being the O₂ evolving complex (OEC) in Photosystem II.⁹ However, a large number of enzymes would implicate Mn, for its sensing and transportation.⁶² To the best of our knoweledge, there has been no well defined biological system in which Mn is coordinated to S-containing ligands. It is characteristic that attempts to coordinate Mn to S(Met) in a molecular variant of the Mn transport regulator of *Bacillus subtilis* were not successful.⁶³ The lack of Mn–S containing biological sites can be explained in terms of unfavorable hard Mn(II)–soft (S) interactions and the pronounced preference of Mn for O- and N-containing ligands. It is of interest to note, that the bond between Mn(II) and the softer (compared to S) Se in complex 7, is the least covalent among the series **4–7**.

The lack of preference of Mn(II) for S-containing ligands, was utilized by nature since the OEC of Photosystem II employs Mn– O chemistry, unimpeded by sulfide reactions, to carry out the H₂O splitting reaction in PSII.⁹ The Mn(II)S₄ core of complex **4** was once considered to resemble in some aspects the Fe(III)S₄ active site in rubredoxins, since it has the same electronic configuration (high-spin 3d⁵).⁶⁴ However, there are certainly critical differences between the two sites. For example, the high covalency of Fe(III)–S bonds in rubredoxin is considered one of the factors that would control the reduction potential of the Fe centre, and hence its electron transfer reactivity.⁵⁹⁶

Conclusions and perspectives

In this work, a detailed theoretical study of the electronic properties of the $R_2P(S)NHP(S)R'_2$ ligands (LH) is presented. The structural changes that take place upon deprotonation of LH, as well as the subsequent enhancement of π delocalization among the SPNPS fragments, are elucidated by well known computational methods.

In addition, new ML₂ complexes of Co(II) and Mn(II) containing these ligands are synthesized in order to complete the whole series M[R₂P(S)NP(S)R'₂]₂, R, R' = Ph and/or 'Pr. Combination of spectroscopic data and theoretical calculations on the ML₂ (M = Mn, Co) complexes, reveal a higher ionic character of the Mn–S bonds compared to Co–S. The CoL₂ complexes are shown to contain Co–S bonds of considerable covalent character. This aspect is rather general, irrespective of the specific nature of their coordination sphere, since similar behaviour has been observed in previously described Co(II)S₄ containing complexes. Therefore, it is expected that it will also manifest itself in the active sites of Co(II)–S containing enzymes or "maquettes".

The relative covalencies of the M–S bonds (M = Mn, Co) in complexes 1–7 are currently being addressed by more direct experimental techniques, such as XAS and EPR/ENDOR spectroscopy. Our common efforts are also focused on the study of the magnetic and spectroscopic properties of the corresponding NiL₂ complexes. (P. Kyritsis, N. Robertson *et al.*, in preparation).

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