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A Tunable Coordination Response of the Phosphorus-Based Hexadentate Ligand (S)P[N(Me)N=CHC$_6$H$_4$-*o*-OH]$_3$ (LH$_3$): Synthesis and Structure of LM (M = Sc, Cr, Mn, Fe, Co, Ga)

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The multidentate ligand (S)P[N(Me)N=CHC$_6$H$_4$-*o*-OH]$_3$ (LH$_3$) reacts with a number of M^{III} salts to afford the neutral mononuclear complexes LM (M = Sc, Cr, Mn, Fe, Co and Ga). The coordination behaviour of the ligand is hexadentate in all of these complexes, where it encapsulates the metal ion in a facial 3N,3O coordination mode. All the metal complexes have been characterised by spectroscopic and X-ray crystallographic methods. The metal atoms in the complexes LSc, LMn, LFe and LGa adopt a distorted octahedral geometry, whereas the geometries of LCr and LCo are more ideal. The electrochemical behaviour of LMn shows that it can be reversibly reduced ($E_{1/2}$ = –0.13 V) in a single electron process. The achiral ligand LH$_3$ induces chirality in the metal complexes LM upon coordination with the metal ion. All the complexes crystallise as racemic compounds where both the clockwise (Δ) and anticlockwise (Λ) enantiomorphs are present in the crystal structure in an ordered arrangement. Furthermore, all complexes show supramolecular chiral recognition in their crystal structures; the Δ form recognizes the Λ form by means of intermolecular C–H···O and C–H···S interactions.

Introduction

Pyrazolylborates, commonly known as scorpionates, are an extremely versatile family of ligands and have found wide use in various aspects of coordination and organometallic chemistry.[1] These ligands are prepared in an essentially modular manner, and the boron atom itself has no role in coordination but is used as a structural anchor to support multiple coordinating pyrazolyl arms.[1] The coordination properties of the pyrazolyl unit can be tuned electronically and sterically before they are attached to the boron atom.[1] Other types of tridentate ligands that have received attention include triamidosilanes and triamidomethanes, which function as trianionic ligands upon deprotonation.[2]

In view of the versatility of the pyrazolylborates the extension of the scorpionate ligand methodology to othernon-boron-containing central atoms has been investigated, although sporadically, with the greatest success being found with the carbon analogues.[3] We have investigated the phosphorus pyrazolides (O)P(3,5-Me$_2$Pz)$_3$, MeP(S)(3,5-Me$_2$Pz)$_2$ or PhP(O)(3,5-Me$_2$Pz)$_2$ with mixed success – on many occasions we have observed that these ligands are hydrolytically sensitive upon interaction with metal ions.[4] On the other hand, phosphorus hydrazides such as (S)P[N(Me)-NH$_2$]$_3$ are quite stable and contain three hydrazide arms with terminal reactive NH$_2$ groups[5–7] that can be elaborated by the efficient click synthetic methodology to afford multidentate coordinating ligands.[7] Accordingly, we have prepared (S)P[N(Me)N=CHC$_6$H$_4$-*o*-OH]$_3$ (LH$_3$; **1**) and have found that interaction of this ligand with M^{II} salts of many first-row transition metals leads to the formation of trinuclear coordination complexes.[7a–7c] Continuing this investigation with M^{III} salts we have noticed that the coordination response of LH$_3$ changes, and mononuclear complexes with a spherical topology are formed. Thus, it is possible to solicit a varied coordination response from the same ligand by varying the oxidation state of the metal ion. Herein we report the synthesis and structural characterisation of the neutral mononuclear complexes LM [M = Sc (**2**), Cr (**3**), Mn (**4**), Fe (**5**), Co (**6**), Ga (**7**)]. The gallium complex **7** shows interesting photoluminescent properties in solution and in the solid state.

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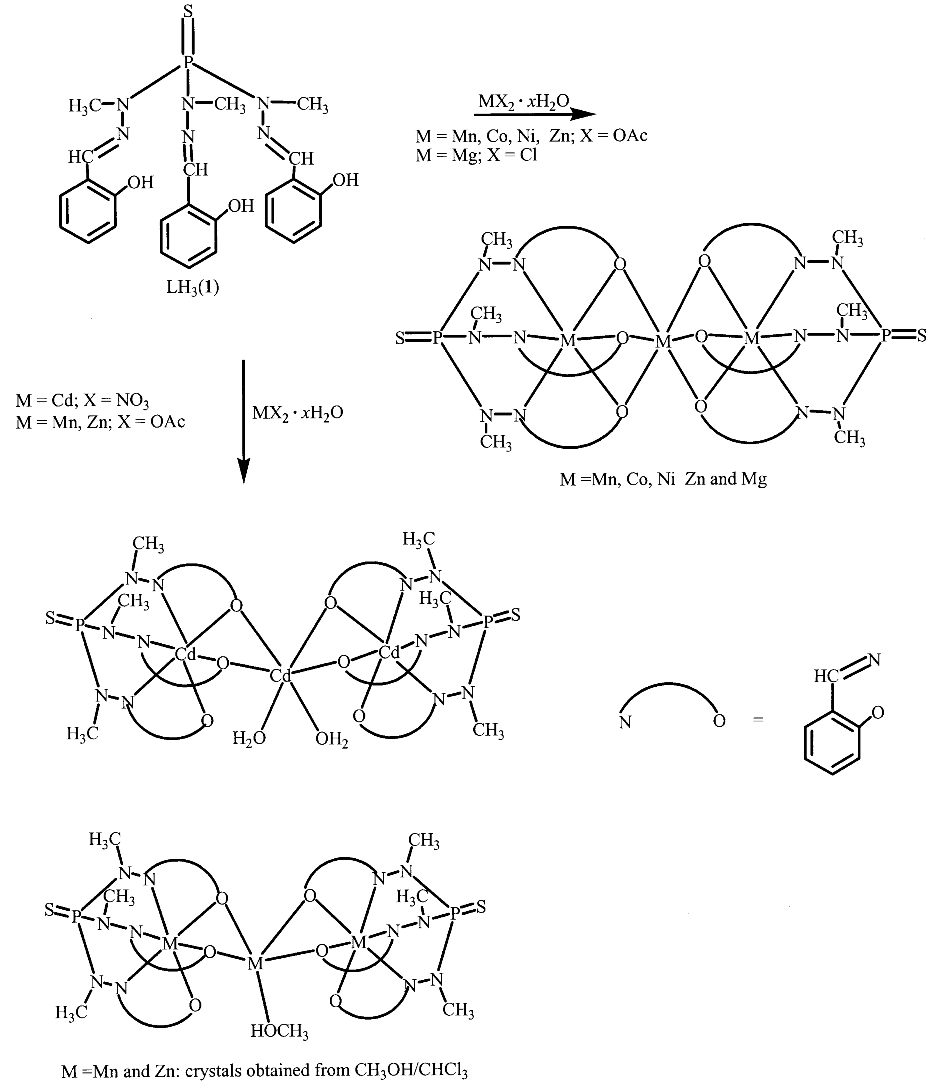
Results and Discussion

Synthesis, Spectroscopy and Electrochemistry

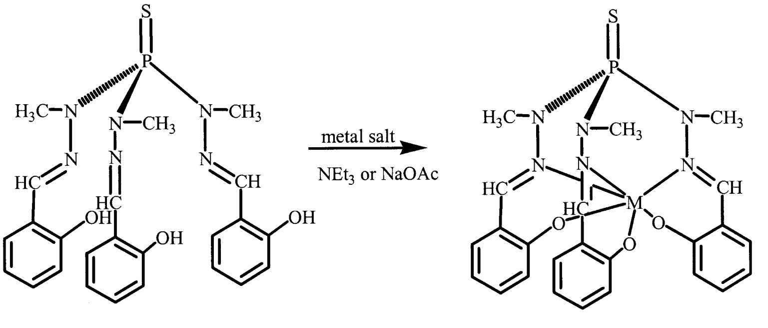
The phosphorus-supported tripodal ligand P(S)[N(Me)-N=CHC$_6$H$_4$-*o*-OH]$_3$ (LH$_3$; **1**) was synthesised as reported previously by condensation of P(S)[N(Me)NH$_2$]$_3$ with salicylaldehyde in a 1:3 ratio. Treatment of LH$_3$ with several divalent transition metal salts has previously afforded neutral trinuclear complexes of the type L$_2$M$_3$ (M = Mn, Co, Ni, Zn, Cd and Mg; Scheme 1).[7a–7c] The arrangement of the three metal atoms is predominantly linear in these complexes. The two terminal metal atoms have a 3N,3O coordination environment, while the central metal atom has a 6O coordination environment. In contrast to the above situation, treatment of LH$_3$ with the first-row transition metal salts Sc(O$_3$SCF$_3$)$_3$, [Cr(H$_2$O)$_4$Cl$_2$]Cl·2H$_2$O, Mn(CH$_3$COO)$_3$·2H$_2$O, Fe(ClO$_4$)$_2$·6H$_2$O, Co(C$_5$H$_7$O$_2$)$_3$ and Ga(NO$_3$)$_3$·*x*H$_2$O under various experimental conditions (see Experimental Section) yielded the stable neutral mononuclear complexes LM [M = Sc (**2**), Cr (**3**), Mn (**4**), Fe (**5**),Co (**6**) and Ga (**7**); Scheme 2]. The metal is present in a formal oxidation state of +3 in all these complexes.

In accordance with the protocol for the synthesis of octahedral chromium complexes, we first reduced CrCl$_3$·6H$_2$O with a small amount of activated granulated zinc in acetonitrile to convert the inert Cr^{III} species into a labile Cr^{II} intermediate which, upon reaction with **1**, yielded LCr (**3**) in very good yield. The complex LFe was obtained by the reaction of LH$_3$ with Fe(ClO$_4$)$_2$·6H$_2$O in the presence of sodium acetate. In this instance, Fe^{II} was converted into Fe^{III} by aerial oxidation.

Complexes **2**–**7** show characteristic molecular-ion peaks in their FAB mass spectra (see Experimental Section). The ^{31}P{^{1}H} NMR spectra of the diamagnetic complexes LSc, LCo and LGa show singlets at δ = 69.9, 76.2 and 64.2 ppm, respectively. These chemical shifts may be compared to that of the parent ligand, which resonates at δ = 71.7 ppm. The NC*H*$_3$ signals for the diamagnetic complexes LSc, LCo and LGa are shifted downfield relative to that of LH$_3$.



Scheme 1.



LH_3 (**1**)

M = Sc (**2**); M^{III} salt: $Sc(CF_3SO_3)_3$
M = Cr (**3**); M^{III} salt: $[Cr(H_2O)_4Cl_2]Cl·2H_2O$
M = Mn (**4**); M^{III} salt: $Mn(CH_3COO)_3·2H_2O$
M = Fe (**5**); M^{III} salt: $Fe(ClO_4)_2·6H_2O$
M = Co (**6**); M^{III} salt: $Co(C_5H_7O_2)_3$
M = Ga (**7**); M^{III} salt: $Ga(NO_3)_3·xH_2O$

Scheme 2.

The high-spin nature of both LMn (**4**) and LFe (**5**) was determined from their magnetic moments [LMn: μ_{eff} (300 K) = 4.78 μ_B; LFe: 5.92 μ_B], which are in agreement with the expected spin-only values for these compounds.

Intense d–d transitions are observed in the UV/Vis spectra of complexes **3** and **4**. The transition observed at 572 nm (ε = 643 $M^{-1}cm^{-1}$) for **3** can be assigned to a $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition and that at 435 nm (ε = 6770 $M^{-1}cm^{-1}$) to a $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transition. The manganese complex **4** shows one d–d transition ($^5E_g \rightarrow {}^5T_{2g}$) at 646 nm ($\varepsilon$ = 750 $M^{-1}cm^{-1}$; see Figure S1 in the Supporting Information). These values are similar to those observed for related Cr^{III} and Mn^{III} complexes reported in the literature.[8] The electronic spectrum of the high-spin octahedral Fe^{III} complex LFe shows an intense band in the visible region at 516 nm (ε = 5461 $M^{-1}cm^{-1}$), which corresponds to an LMCT (phenolato oxygen → iron) transition.

We also investigated the photoluminescence behaviour of the diamagnetic complexes LSc, LCo and LGa since the trinuclear metal complexes L_2Mg_3[7b] and L_2Cd_3[7c] show such a behaviour. The ligand LH_3 does not show any fluorescence. Of these three diamagnetic complexes, only LGa showed fluorescence both in solution and in the solid state. The emission spectra of LGa in solution (CH_2Cl_2; λ_{ex} = 362 nm) and in the solid state (λ_{ex} = 362 nm) are shown in Figure S2 (see Supporting Information). An intense emission with a peak maximum at 465 nm is observed in dichloromethane solution, whereas the solid-state emission peak occurs at 458 nm. The luminescence behaviour of LGa compares favourably with that observed for the trinuclear complexes mentioned above.[7b,7c]

The X-band EPR spectra of LCr in the solid state, both at room temp. and 120 K, show one sharp, isotropic signal at g = 1.99, which is typical of a Cr^{III} (d^3, I = 3/2) system (see Figure S3 in the Supporting Information).[9] The spectrum is not very well resolved in solution at room temperature (dichloromethane/toluene). At 120 K (dichloromethane/toluene glass), however, the spectrum is more resolved and shows an axial pattern ($g_{\parallel}$ = 2.04 and $g_{\perp}$ = 1.99) (Figure S3 in the Supporting Information).

We were not able to observe a good X-band EPR spectrum for LMn. This may be due to the high-spin nature of the Mn^{III} ion resulting in an S = 2 spin ground state,[10] which should result in a large zero-field splitting. The absence of EPR signals at X-band frequencies is expected for such systems if the zero-field splitting is much larger than the microwave quantum used in the spectrometer. The EPR spectrum of the high-spin d^5 complex LFe (S = 5/2) in CH_2Cl_2/toluene glass at 120 K shows resonances in the low-field region (peak at g = 4.25) and a relatively broad absorption in the range g = 9.0–4.0 (see Figure S4 in the Supporting Information). This is typical of high-spin iron(III) complexes where the metal atom is present in a rhombically distorted low symmetry position. In this instance, the zero-field splitting terms remove the degeneracy of the spin sextet and result in three Kramer's doublets; transitions within these states give rise to resonances in the low-field region of the spectra.[11]

The electrochemical behaviour of the manganese complex LMn is interesting. This complex is reversibly reduced ($E_{1/2}$ = –0.13 V) and oxidized ($E_{1/2}$ = +0.63 V) in a single-electron process [Equation (1) and Figure 1]. This clearly

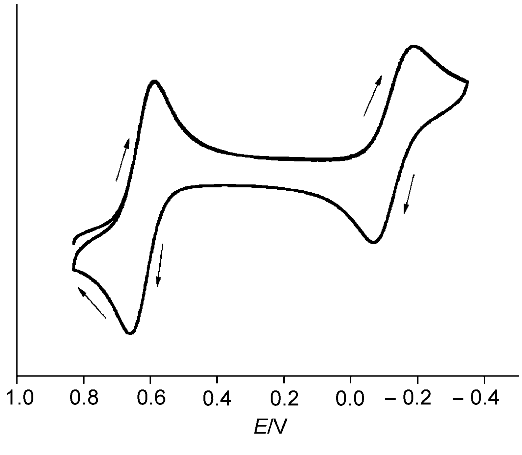


Figure 1. Cyclic voltammogram of LMn in CH_2Cl_2 recorded against Ag/AgCl. Scan rate: 100 mV s^{-1}.

gives an indication that the phosphorus-supported tripodal anionic ligand L^{3-} is able to stabilize various oxidation states of transition metal ions, including the Mn^{IV} oxidation state.

$$[LMn^{IV}]^+ \underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}} [LMn^{III}] \underset{-\,e^-}{\overset{+\,e^-}{\rightleftharpoons}} [LMn^{II}]^- \tag{1}$$

X-ray Crystal Structures of 2–7

Complexes **2**–**7** are isostructural, and the ORTEP diagrams of some representative examples (**2**, **4** and **6**) are shown in Figures 2, 3 and 4, respectively. The ORTEP diagrams for the remaining complexes are available as Supporting Information (Figures S5–S7). Table S1 (Supporting Information) provides a summary of the metric parameters of **2**–**7** and the X-ray crystallographic data are summarised in the Experimental Section (Tables 1 and 2).

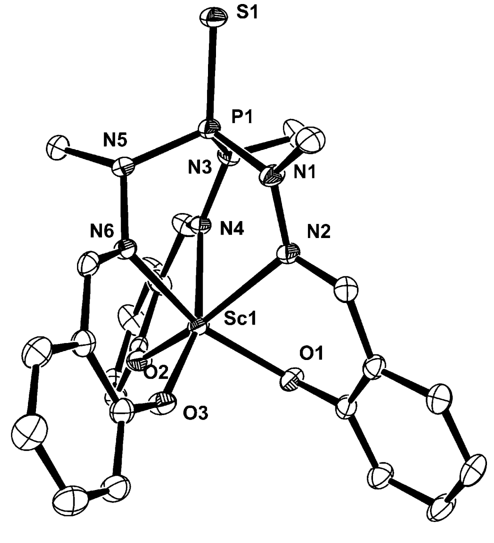


Figure 2. ORTEP diagram of LSc (**2**). All the hydrogen atoms have been omitted for clarity.

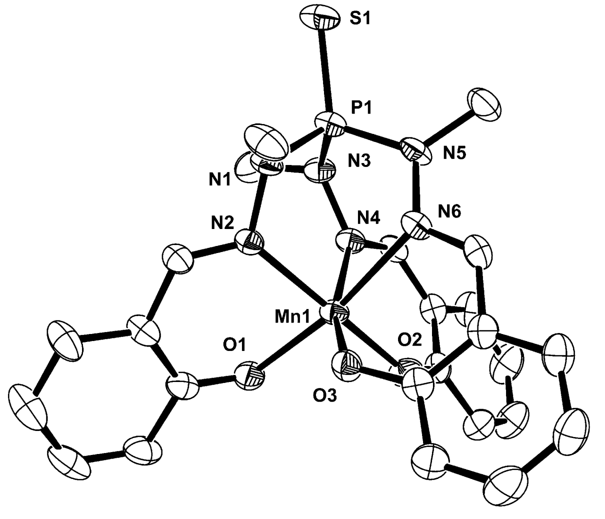


Figure 3. ORTEP diagram of LMn (**4**). All the hydrogen atoms have been omitted for clarity.

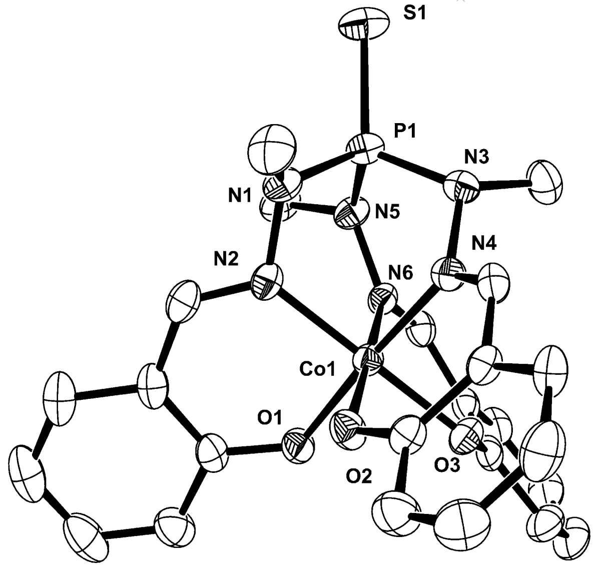


Figure 4. ORTEP diagram of LCo (**6**). All the hydrogen atoms have been omitted for clarity.

The metal ions in all the complexes have an identical coordination environment (formed by a 3N,3O donor set comprising three facial imino nitrogen atoms and three phenolate oxygen atoms) derived from the triply deprotonated tripodal ligand L^{3-} (Figures 2, 3, 4, and 5). The metal atoms in the complexes LSc, LMn, LFe and LGa adopt a distorted octahedral geometry, whereas complexes LCr and LCo have a more ideal geometry. The extent of this distortion can be gauged by the deviation of bond angles from the ideal geometry. For example, the O2–Sc1–N2, O1–Sc1–N6 and O3–Sc1–N4 bond angles in LSc are 161.34(5)°, 151.57(5)° and 160.17(5)°, respectively, and show a considerable deviation from the ideal 180° bond angle (Table S1 in the Supporting Information). A similar feature is also found for LMn, LFe and LGa. All the metal complexes possess a spherical topology with the metal centre encapsulated by the hexadentate ligand. As a result of the multidentate coordination of the ligand in these LM complexes, each metal atom forms part of six six-membered metallacycles.

The metric parameters found in the immediate coordination environment around **2**–**7** are summarised in Table S1 in the Supporting Information. A comparison of the average bond parameters in these complexes along with that of LH_3 is provided in Table S2 (see Supporting Information). There is a slight increase in the N–N bond length in the complexes relative to that found in LH_3 due to the coordination of the imino nitrogen atom to the metal ion. On the other hand, there is no appreciable change in the C=N bond length. In general, the M–N bonds are slightly longer than the M–O bonds. In the case of **6**, however, both M–N and M–O bond lengths are similar.

The high-spin Mn^{III} ion in LMn (**4**) displays a Jahn–Teller distortion. The coordination environment around this manganese ion is shown in Figure 5. The mutually *trans*-axial Mn–N(6) and Mn–O(1) distances are longer than the Mn–N and Mn–O distances in the equatorial

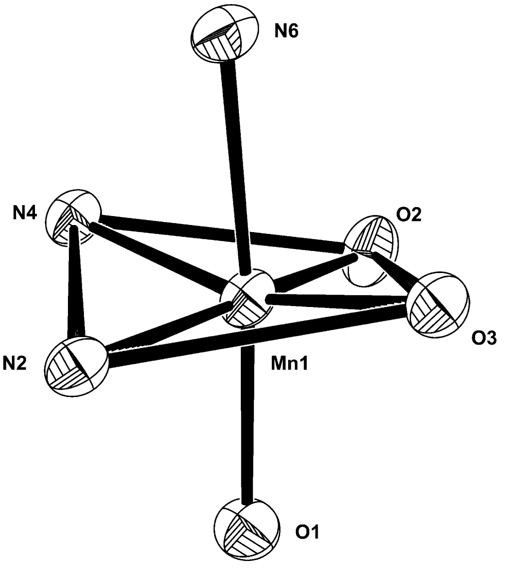


Figure 5. Coordination environment around the Mn^{III} centre in LMn (**4**). Selected bond lengths [Å]: Mn(1)–O(2) 1.878(2), Mn(1)–O(3) 1.9004(17), Mn(1)–N(4) 2.040(2), Mn(1)–O(1) 2.060(2), Mn(1)–N(2) 2.065(2), Mn(1)–N(6) 2.328(2).

plane, with the $Mn–N_{axial}$ distance being 0.28 Å longer than the average $Mn–N_{eq}$ distance. This difference is about 0.17 Å for the Mn–O distances.

It is interesting to compare the bond lengths found for the M^{III} complexes formed with LH_3 with the corresponding M^{II} complexes (see Table S3 in the Supporting Information), which are trinuclear. However, the terminal metal atoms in the latter also possess a 3N,3O coordination environment, and hence a comparison between these two situations is possible. The three Mn–N and Mn–O distances in L_2Mn_3 are similar [av. 2.245(10) and 2.133(8) Å, respectively], while in LMn, as noted above, there are substantial differences in the $Mn–X_{ax}$ and $Mn–X_{eq}$ bond lengths (X = N or O). Unfortunately, the Jahn–Teller distortion at Mn^{III} in LMn does not allow the impact of the change of oxidation state of the metal on the metric parameters to be assessed, although this is possible in the complexes LCo and L_2Co_3. The average Co–N and Co–O bond lengths in the former are 1.914(3) and 1.898(2) Å, respectively, whereas in the latter, as anticipated, these values increase to 2.116(4) and 2.070(3) Å respectively (Table S3 in the Supporting Information).

Stereochemistry

The stereochemistry of the tripodal ligand LH_3 at the molecular and supramolecular level is quite interesting. The ligand is achiral and possesses C_3 symmetry, with the molecular C_3 axis passing through the S=P bond. The ligand induces chirality [Δ (clockwise) and Λ (anticlockwise)] in the LM complexes due to a screw-type coordination arrangement (Figure 6).[7c,12,13] It is known that when a chiral molecule is formed from achiral precursors it is always a racemate (a mixture of equal amounts of both the mirror images or the left- and right-handed configurations of a compound). A racemate is known to crystallise in three ways: (1) to generate a *racemic compound*, where both the

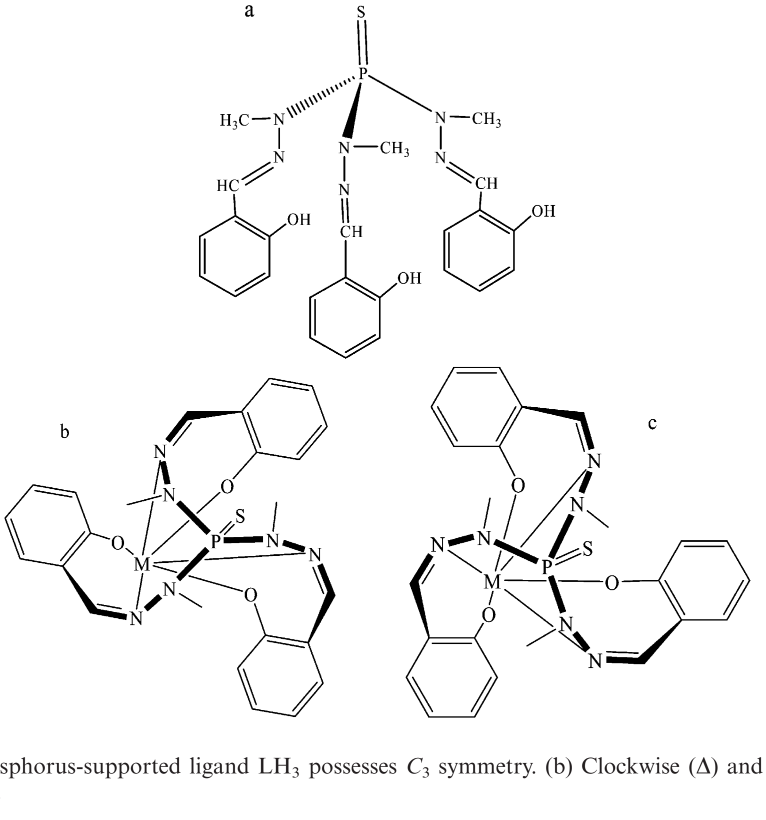


Figure 6. (a) The achiral phosphorus-supported ligand LH_3 possesses C_3 symmetry. (b) Clockwise (Δ) and (c) anticlockwise forms (Λ) of the enantiomorphs of LM.

enantiomers are present in every crystal in an ordered arrangement; (2) to generate a *conglomerate*, where the two enantiomers crystallise out separately (this process is in fact spontaneous resolution under crystallisation conditions);[14,15] and (3) to generate a *pseudo-racemate*, where both the enantiomers are present in every crystal in a disordered arrangement. In the present instance all the complexes crystallise as racemic compounds where both the clockwise and anticlockwise forms are present in the crystal structure in an ordered arrangement.

All the mononuclear complexes **2**–**7** show supramolecular chiral recognition in their crystal structures (Figure 7 and Figures S8–S15 in the Supporting Information). Thus, in all instances, although the nature of the eventual supramolecular formation is different, the Δ form recognizes the Λ form and forms supramolecular bonds with it involving intermolecular C–H···O and C–H···S interactions. In the case of C–H···O interactions, the phenolate oxygen atoms act as proton acceptors, whereas in the case of C–H···S interactions the P=S unit acts as a proton acceptor. As a representative example, the supramolecular formation found in the crystal structure of LCr is shown in Figure 7. In this instance, a honeycomb-like (6,3)-network mediated by the C–H···O interactions is found. The bond parameters involved in these interactions are given in Table S4 (see the Supporting Information).

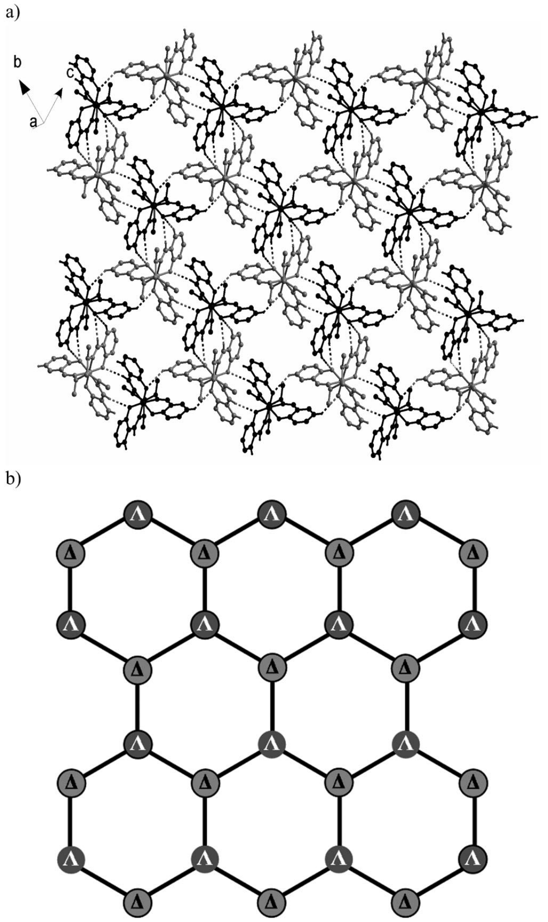


Figure 7. (a) Honeycomb-like (6,3)-network mediated by the C–H···O interactions (dotted lines) in LCr (**3**). (b) Representation of the honeycomb network showing the chiral recognition found in the assembly.

Conclusions

The phosphorus-supported multi-site ligand LH_3 functions as a trianionic hexadentate ligand when forming neutral mononuclear complexes of the type LM. This is in contrast to the previously studied examples where L_2M_3-type linear trinuclear complexes were isolated, which suggests a tunability of the coordination response of LH_3 depending on the nature of the metal ion. The screw-type geometry imposed by the ligand in the LM complexes allows them to crystallise as racemates that show chiral recognition in their solid-state structures. The versatile coordination behaviour of LH_3 and the modular nature of its synthesis suggest that such phosphorus-supported ligands can be expanded into an attractive library of multidentate ligands.

Experimental Section

Reagents and General Procedures: Solvents were purified by conventional methods and freshly distilled under nitrogen prior to use according to standard procedures.[16] (S)PCl_3, salicylaldehyde, $Sc(CF_3SO_3)_3$ and $Co(C_5H_7O_2)_3$ were purchased from Fluka (Switzerland) and used as such. $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$, $Mn(CH_3COO)_3\cdot 2H_2O$ and $Ga(NO_3)_3\cdot XH_2O$ were purchased from Aldrich Chemicals (USA) and used as received. $Fe(ClO_4)_2\cdot 6H_2O$ was freshly prepared prior to the metallation reaction. *N*-Methylhydrazine was obtained as a gift from the Vikram Sarabhai Space Research Centre, Thiruvananthapuram, India and was used as such.

Caution! *Perchlorate salts are potentially explosive. They should be handled with great care with appropriate precautions.*

Instrumentation: Electronic spectra were recorded with a Perkin–Elmer Lambda 20 UV/Vis spectrometer or a Shimadzu UV-160 spectrometer with dichloromethane as the solvent. IR spectra were recorded as KBr pellets with a Bruker Vector 22 FT IR spectrophotometer in the range 400–4000 cm^{-1}. Elemental analyses of the compounds were obtained with a Thermoquest CE instruments CHNS-O, EA/110 model. FAB mass spectra were recorded with a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded for $CDCl_3$ solutions with a JEOL JNM LAMBDA 400 model spectrometer operating at 400.0 and 161.7 MHz, respectively. Chemical shifts are reported in ppm with respect to internal tetramethylsilane (^1H) and external 85% H_3PO_4 (^{31}P) as the references. The electrochemistry of the complexes was studied with a BAS Epsilon electrochemical workstation. Cyclic voltammetry (CV) and differential pulse voltammograms (DPV) were recorded for dichloromethane solutions containing 0.10 M tetra-*n*-butylammonium hexaflurophosphate as supporting electrolyte. The concentration of the complexes was typically of the order of 10^{-3} M. The CV scans were recorded against Ag/AgCl with a scan rate of 100 $mV\,s^{-1}$.

X-ray Crystallography: The crystal data and parameters for complexes **2**–**7** are given in Tables 1 and 2. Single crystals of **2**–**5** and **7**

suitable for X-ray crystallographic analyses were obtained by slow concentration of their dichloromethane solutions, whereas crystals of **6** were obtained by vapour diffusion of *n*-hexane into its chloroform solution. All the crystals of **2**–**7** lose their solvent of crystallisation rapidly when taken out of the mother liquor at room temperature. The crystal data for **2**, **3** and **7** were collected with a Bruker Smart Apex Diffractometer and those of **4**–**6** with a Stoe IPDS machine. All structures were solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares methods against F^2 with SHELXL-97.[17] Hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. CCDC-659600, -659601, -659602, -659603 and -659604, -659605 (for complexes **2**–**7**, respectively) contain the supplementary crystallographic data for this publication. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Measurements: The magnetisations of powdered samples of **3**–**6** were assessed by SQUID (superconducting quantum interference device) measurements, using a Quantum Design MPMS-5 magnetometer, at room temperature (300 K) in a constant field of 1 T. The data were corrected for the sample holder, and diamagnetic corrections were based on the experimentally derived susceptibility of the diamagnetic analogue LCo [$CoC_{24}H_{24}N_6O_3PS$] (**6**; $\chi_{dia} = -1.9881 \times 10^{-5}$ emu mol^{-1}).

P(S)[N(Me)N=CH-C_6H_4-*o*-OH]$_3$ (LH$_3$; 1): Compound **1** was synthesised according to a procedure reported in the literature.[7a]

LSc (2): A solution of scandium triflate (0.197 g, 0.400 mmol) in methanol (30 mL) was added dropwise to a solution of ligand **1** (0.204 g, 0.400 mmol) and triethylamine (0.3 mL, 2.0 mmol) in chloroform (30 mL) at room temperature and the mixture stirred for 6 h. The solution was then concentrated to dryness and the residue obtained washed twice with cold methanol to remove any unreacted scandium triflate. The resultant solid was dissolved in dichloromethane and this solution allowed to concentrate slowly to give a crystalline product. Yield: 0.06 g (27.2 %). M.p. > 280 °C. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 314 (1.13×10^4), 285 (4.4×10^4 M^{-1} cm^{-1}) nm. FT-IR: $\nu_{C=N}$ = 1597 cm^{-1}. ^{1}H NMR: δ = 3.11 [d, $^3J_{H,P}$ = 10.0 Hz, 9 H, N(C*H*$_3$)], 6.65–7.18 (m, 13 H, aromatic + imino) ppm. ^{31}P NMR: δ = 70.0 (s) ppm. FAB-MS: *m*/*z* = 552 [M$^+$]. $C_{24}H_{24}N_6O_3PSSc$ (552.48): calcd. C 52.17, H 4.38, N 15.22; found C 51.96, H 4.24, N 15.02.

LCr (3): A small amount of activated granulated zinc was added to a suspension of [$Cr(H_2O)_4Cl_2$]Cl·2H_2O (0.093 g, 0.350 mmol) and **1** (0.179 g, 0.350 mmol) in acetonitrile and the mixture refluxed in air for 30 min, during which time the solution turned pink. Triethylamine (0.5 mL, 3.5 mmol) was added, and the reaction mixture was refluxed for a further 6 h. Removal of the solvent from the reaction mixture afforded a residue, which was washed twice with cold methanol to remove the triethylamine hydrochloride. The remaining portion was dissolved in a minimum amount of dichloromethane (5 mL), *n*-hexane was added until a slight turbidity appeared, and it was then stored at 5 °C to obtain crystals of **3**. Yield: 0.17 g (85.0 %). M.p. > 280 °C. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 572 (643), 435 (6.77×10^3), 393 (1.22×10^4), 295 (2.80×10^4), 236 (5.03×10^4 M^{-1} cm^{-1}) nm. FT-IR: $\nu_{C=N}$ = 1601 cm^{-1}. FAB-MS: *m*/*z* = 560 [M$^+$]. μ_{eff} (300 K) = 3.91 μ_B. $C_{24}H_{24}CrN_6O_3PS$ (559.52): calcd. C 51.52, H 4.32, N 15.02; found C 50.90, H 4.14, N 14.88.

LMn (4): A solution of manganese(III) acetate (0.054 g, 0.2 mmol) in methanol (30 mL) was added dropwise to a solution of **1** (0.102 g, 0.200 mmol) and triethylamine (0.3 mL, 2.0 mmol) in

Table 1. Crystallographic data and structure refinement details for complexes **2**–**4**.

	LSc (**2**)	LCr (**3**)	LMn (**4**)
Empirical formula	$C_{25.5}H_{27}Cl_3N_6O_3PSSc$	$C_{26}H_{28}Cl_4CrN_6O_3PS$	$C_{25.5}H_{27}Cl_3MnN_6O_3PS$
Formula mass	679.87	729.37	689.85
Temperature [K]	100(2)	100(2)	213(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.0455(11)	11.3524(7)	11.316(2)
b [Å]	12.3019(12)	12.3856(7)	12.448(3)
c [Å]	13.0714(13)	12.6941(7)	13.157(3)
α [°]	108.965(3)	69.974(10)	110.19(3)
β [°]	106.777(10)	66.807(10)	108.04(3)
γ [°]	104.643(10)	88.229(10)	105.57(3)
V [Å^3]	1485.9(3)	1530.22(15)	1500.6(5)
Z	2	2	2
Crystal size [mm]	0.6 × 0.5 × 0.4	0.8 × 0.6 × 0.6	0.5 × 0.4 × 0.3
$D_{calcd.}$ [g cm^{-3}]	1.520	1.583	1.527
μ [mm^{-1}]	0.681	0.884	0.869
F(000)	698	746	706
θ range [°]	1.80–25.03	1.76–28.28	1.94–24.10
Limiting indices	$-12 \le h \le 13$ $-14 \le k \le 14$ $-15 \le l \le 15$	$-14 \le h \le 10$ $-16 \le k \le 16$ $-16 \le l \le 16$	$-12 \le h \le 12$ $-14 \le k \le 14$ $-15 \le l \le 14$
Reflections collected	7478	9533	9424
Independent reflections	5138 (R_{int} = 0.0140)	6679 (R_{int} = 0.0126)	4387 (R_{int} = 0.0368)
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	5138/0/373	6679/0/382	4387/23/380
Goodness-of-fit on F^2	1.029	1.068	1.059
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0289, wR_2 = 0.076	R_1 = 0.0333, wR_2 = 0.0855	R_1 = 0.0378, wR_2 = 0.1007
R indices (all data)	R_1 = 0.0311, wR_2 = 0.0748	R_1 = 0.0347, wR_2 = 0.0864	R_1 = 0.0420, wR_2 = 0.1051

Table 2. Crystallographic data and structure refinement details for compound **5**–**7**.

	LFe (**5**)	LCo (**6**)	LGa (**7**)
Empirical formula	$C_{26}H_{28}Cl_4FeN_6O_3PS$	$C_{25}H_{25}Cl_3CoN_6O_3PS$	$C_{26}H_{28}Cl_4GaN_6O_3PS$
Formula mass	733.22	685.82	747.09
Temperature [K]	213(2)	213(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.406(2)	11.381(2)	11.3540(8)
b [Å]	12.462(3)	12.087(2)	12.3854(8)
c [Å]	12.799(3)	12.859(2)	12.7008(9)
α [°]	70.94(3)	74.96(2)	70.0940(10)
β [°]	67.33(3)	72.37(2)	66.9830(10)
γ [°]	88.71(3)	62.724(18)	88.2670(10)
V [Å^3]	1575.4(6)	1483.2(4)	1534.67(18)
Z	2	2	2
Crystal size [mm]	0.4 × 0.4 × 0.4	0.3 × 0.3 0.1	0.6 × 0.5 × 0.2
$D_{calcd.}$ [g cm^{-3}]	1.546	1.536	1.617
μ [mm^{-1}]	0.974	1.012	1.406
F(000)	750	700	760
θ range [°]	1.84–24.03	1.68–24.18	1.76–25.02
Limiting indices	$-13 \leq h \leq 12$ $-13 \leq k \leq 14$ $-14 \leq l \leq 14$	$-13 \leq h \leq 12$, $-13 \leq k \leq 13$ $-14 \leq l \leq 14$	$-12 \leq h \leq 13$ $-14 \leq k \leq 13$ $-15 \leq l \leq 9$
Reflections collected	9851	9402	7969
Independent reflections	4603 (R_{int} = 0.0647)	4377 (R_{int} = 0.0476)	5302 (R_{int} = 0.0476)
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	4603/0/382	4377/0/364	5302/0/382
Goodness-of-fit on F^2	1.059	0.968	1.051
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0508, wR_2 = 0.1330	R_1 = 0.0387, wR_2 = 0.0974	R_1 = 0.0347, wR_2 = 0.0967
R indices (all data)	R_1 = 0.0563, wR_2 = 0.1382	R_1 = 0.0511, wR_2 = 0.1021	R_1 = 0.05361, wR_2 = 0.0975

chloroform (30 mL) at room temperature and the mixture stirred for 6 h. A dark green metal complex precipitated from the reaction mixture and was filtered off. This precipitate was dissolved in a minimum amount of dichloromethane (5 mL), *n*-hexane was added until a slight turbidity appeared, and it was then stored at 5 °C to obtain a crystalline product. Yield: 0.08 g (71.2%). M.p. >280 °C. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 646 (750), 432 (6.89×10^3), 334 (1.72×10^4), 275 (2.89×10^4), 244 (4.99×10^4 M^{-1} cm^{-1}) nm. FT-IR: $\nu_{C=N}$ = 1601 cm^{-1}. ^{31}P NMR: δ = –115.2 (s) ppm. FAB-MS: m/z = 562 [M$^+$]. μ_{eff} (300 K) = 4.78 μ_B. $C_{24}H_{24}MnN_6O_3PS$ (562.46): calcd. C 51.25, H 4.30, N 14.94; found C 51.40, H 4.24, N 14.90.

LFe (5): Anhydrous sodium acetate (0.049 g, 0.600 mmol) was added to a solution of **1** (0.102 g, 0.200 mmol) and $Fe(ClO_4)_2 \cdot 6H_2O$ (0.073 g, 0.200 mmol) in chloroform (30 mL) and methanol (30 mL) and the mixture stirred for 6 h. A dark red metal complex precipitated from the reaction mixture and was filtered off. This precipitate was dissolved in a minimum amount of dichloromethane (5 mL), *n*-hexane was added until a slight turbidity appeared, and it was then stored at 5 °C to obtain crystals of **5**. Yield: 0.09 g (80.0%). M.p. >280 °C. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 516 (5.46×10^3), 365 (1.59×10^4), 280 (4.21×10^4), 236 (5.64×10^4 M^{-1} cm^{-1}) nm. FT-IR: $\nu_{C=N}$ = 1598 cm^{-1}. FAB-MS: m/z = 564 [M$^+$]. μ_{eff} (300 K) = 5.92 μ_B. $C_{24}H_{24}FeN_6O_3PS$ (563.37): calcd. C 51.17, H 4.29, N 14.91; found C 50.90, H 3.94, N 14.78.

LCo (6): The same procedure as described for the preparation of **5** was employed, except that cobalt(III) acetylacetonate (0.071 g, 0.200 mmol) was used as the metal precursor. Yield: 0.09 g (80.0%). M.p. >280 °C. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 409 (1.02×10^4), 307 (1.33×10^4), 256 (6.97×10^4 M^{-1} cm^{-1}) nm. FT-IR: $\nu_{C=N}$ = 1600 cm^{-1}. ^{1}H NMR: δ = 3.08 [d, $^3J_{H,P}$ = 10.7 Hz, 9 H, N(CH_3)], 6.44–6.47 (m, 3 H, aromatic), 6.98–7.01 (m, 6 H, aromatic), 7.09–7.12 (m, 3 H, aromatic), 7.71 (s, 3 H, imino) ppm. ^{31}P NMR: δ = 76.15 (s) ppm. FAB-MS: m/z = 567 [M$^+$]. $C_{24}H_{24}CoN_6O_3PS$ (566.46): calcd. C 50.89, H 4.27, N 14.84; found C 50.60, H 4.06, N 14.58.

LGa (7): A solution of **1** (0.255 g, 0.5 mmol) and triethylamine (0.42 mL, 3 mmol) in chloroform (30 mL) was added dropwise to a solution of hydrated gallium nitrate (0.128 g) in methanol (30 mL) at room temperature. The mixture was stirred for 6 h and then concentrated to dryness. The solid obtained was washed twice with cold methanol to remove any unreacted gallium nitrate and other salts. The residue was dissolved in dichloromethane and allowed to concentrate slowly at room temperature to obtain **7** as a crystalline product. Yield: 0.10 g (34.5%). M.p. >280 °C. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 362 (7355), 310 (23990), 287 (41228 M^{-1} cm^{-1}) nm. FT-IR: $\nu_{C=N}$ = 1603 cm^{-1}. ^{1}H NMR: δ = 3.21 [d, $^3J_{H,P}$ = 10.5 Hz, 9 H, N(CH_3)], 6.60–6.64 (m, 3 H, aromatic), 6.77–6.79 (m, 3 H, aromatic), 7.03–7.05 (m, 3 H, aromatic), 7.19–7.24 (m, 3 H, aromatic), 8.18 (s, 3 H, imino) ppm. ^{31}P NMR: δ = 64.23 (s) ppm. FAB-MS: m/z = 577 [M$^+$]. $C_{24}H_{24}GaN_6O_3PS$ (577.25): calcd. C 49.94, H 4.19, N 14.55; found C 49.76, H 4.10, N 14.28.

Supporting Information (see footnote on the first page of this article): Electronic spectra of LCr, LMn and LFe, fluorescence emission spectra of LGa, X-Band EPR spectra of LCr and LFe, ORTEP diagrams of LCr, LFe and LGa, C–H···O and C–H···S interactions, selected bond lengths and angles for complexes **2**–**7**, comparison of important bond lengths of LH_3 with those of complexes **2**–**7**, comparison of important bond lengths of LMn and LCo with L_2Mn_3 and L_2Co_3, hydrogen bond parameters for LCr, LFe and LGa.

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