

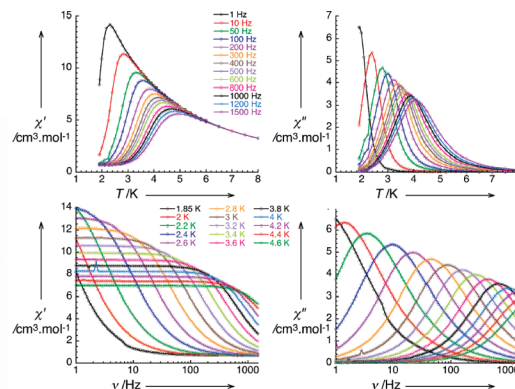
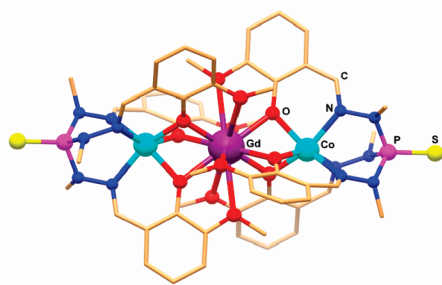
Phosphorus-Supported Ligands for the Assembly of Multimetal Architectures[†]

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CON SPECTUS



Modeled after boron-based scorpionate ligands, acyclic and cyclic phosphorus-containing compounds possessing reactive groups can serve as excellent precursors for the assembly of novel phosphorus-supported ligands that can coordinate multiple sites. In such ligands, the phosphorus atom does not have any role in coordination but is used as a structural support to assemble one or more coordination platforms. In this Account, we describe the utility of inorganic heterocyclic rings such as cyclophosphazenes and carbophosphazenes as well as acyclic phosphorus-containing compounds such as (S)PCl₃, RP(O)Cl₂, and R₂P(O)Cl for building such multisite coordination platforms. We can modulate the number and orientation of such coordination platforms through the choice of the phosphorus-containing precursor. This methodology is quite general and modular and allows the creation of well-defined libraries of multisite coordination ligands. Phosphorus-supported pyrazolyl ligands are quite useful for building multimetallic architectures. Some of these ligands are prone to P–N bond hydrolysis upon metalation, but we have exploited the P–N bond sensitivity to generate *hydrolyzed ligands* in situ, which are useful to build multimetal assemblies. In addition, the intimate relationship between small molecule cyclophosphazenes and the corresponding pendant cyclophosphazene-containing polymer systems facilitated our design of polymer-supported catalysts for phosphate ester hydrolysis, plasmid DNA modification, and C–C bond formation reactions. Phosphorus hydrazides containing reactive amine groups are ideal precursors for integration into more complex ligand systems. The ligand (S)P[N(Me)N=CH-C₆H₄-2-OH]₃ (LH₃) contains six coordination sites, and its coordination response depends upon the oxidation state of the metal ion employed. LH₃ reacts with divalent transition metal ions to afford neutral trimetallic derivatives L₂M₃, where the three metal ions are arranged in a perfectly linear manner in many cases. Incorporating an additional methoxy group into LH₃ affords the ligand (S)P[N(Me)N=CH-C₆H₃-2-OH-3-OMe]₃ (L'H₃), which contains nine coordination sites: three imino nitrogen atoms, three phenolate oxygen atoms, and three methoxy oxygen atoms. The reaction of L'H₃ with transition metal salts in 1:1 ratio leads to the in situ formation of a metalloligand (L'M), which on further treatment with lanthanide salts gives heterobimetallic trinuclear cationic complexes [L'₂M₂Ln]⁺ containing a M–Ln–M linear array (M = transition metal ion in a +2 oxidation state). Many of these 3d–4f compounds behave as single-molecule magnets at low temperatures. Although challenges remain in the development of synthetic methods and in the architectural control of the coordination platforms, we see opportunities for further research into coordination platforms supported by main group elements such as phosphorus. As we have shown in this Account, one potential disadvantage, sensitivity of P–N bonds to hydrolysis, can be used successfully to build larger assemblies.

I. Introduction

Poly(pyrazolyl)borates, more commonly known as scorpionates, are among the most ubiquitous and versatile multidentate ligands.^{1,2} Their applications in coordination and organometallic chemistry are well documented and cover much ground, ranging from synthesis of model compounds that mimic metalloenzymes³ to stabilization of low coordination of main group elements.⁴ One of the main reasons for the success of this family of ligands lies in the fact that their synthesis is essentially modular. Predesigned pyrazolyl coordinating groups with varying steric and electronic features are anchored on a central boron atom in a single-step synthesis. The boron atom functions as an inert (noncoordinating) support for the coordinating groups. It also controls the topological orientation of the pyrazolyl groups. The success of the poly(pyrazolyl)borate family has spurred interest in examining the applicability of its design features to other systems involving carbon,⁵ silicon,⁶ or phosphorus supports.⁷ In view of our interest in inorganic rings, we were interested in applying this modular synthetic methodology for developing a family of cyclophosphazene-based multisite coordination ligands. Very quickly this program was expanded to many other types of phosphorus-supported ligands, and we were able to demonstrate the efficacy of this approach for building a number of multimetal assemblies. This Account focuses, mainly, on our recent efforts on using these new phosphorus-supported multisite coordination ligands for building transition metal aggregates including heterometallic 3d–4f assemblies, some of which have been shown to possess single-molecule magnetism behavior.

II. Cyclophosphazene and Carbophosphazene-Based Ligands and Their Metalation Behavior

II.1. Pyrazolyl Cyclophosphazenes and Cyclophosphazene Hydrazides. Our entry into phosphorus-supported ligands began by considering whether multisite coordination ligands can be built using cyclophosphazenes as supports. Chlorocyclophosphazenes such as $N_3P_3Cl_6$ (**1**), 2,2- $Ph_2N_3P_3Cl_4$ (**2**), 2,2-(NH_2) $_2N_3P_3Cl_4$ (**3**), and 2,2-*spiro*-($C_{12}H_8O_2$) $N_3P_3Cl_4$ (**4**) were utilized as convenient precursors for building multipyrazolyl ligands: $[N_3P_3(DMPz)_6]$ (**5**) (DMPz = 3,5-dimethyl pyrazolyl), $[2,2-Ph_2N_3P_3(DMPz)_4]$ (**6**), $[2,2-(NHCH_2CH_2CH_2NH)N_3P_3(DMPz)_4]$ (**7**), and $[2,2-(NH_2)_2N_3P_3(DMPz)_4]$ (**8**).^{8–10} Monometallic, homobimetallic, and heterobimetallic compounds were readily obtained from these ligands.^{8–11} In all cases, the pyrazolyl nitrogens were effectively used for coordination. Another inter-

esting observation was that metalation increased the hydrolytic sensitivity of the pyrazolyl cyclophosphazene ligands, and in some instances, an in situ P–N bond hydrolysis was observed.⁹ In all cases, the planarity of the cyclophosphazene ring was distorted upon coordination. Also, the P–N bonds flanking the site of coordination underwent elongation in each case.

We were able to extend the small molecule chemistry of the cyclophosphazene ligands to the corresponding macromolecules¹² by making adjustments in the design of the ligand. A multipyrazolyl cyclophosphazene containing a polymerizable group $N_3P_3(3,5-Me_2Pz)_5(O-C_6H_4-p-C_6H_4-p-CH=CH_2)$ (**13**) was copolymerized with divinylbenzene to afford a cross-linked multisite coordinating polymer (**14**), which was readily metalated with $CuCl_2$ to afford the metalated polymer (**15**) (Chart 1).¹³ The latter is an effective heterogeneous catalyst in phosphate ester hydrolysis involving three model phosphate esters: *p*-nitrophenyl phosphate (**16**), bis(*p*-nitrophenyl) phosphate (**17**), and 2-(hydroxyl-propyl)-*p*-nitrophenyl phosphate (**18**) (Chart 2).¹³ The hydrolysis proceeds with significant rate enhancement for all three substrates in comparison to the corresponding uncatalyzed reaction. The highest rate enhancement (2.8×10^5) was observed for bis(*p*-nitrophenyl) phosphate. Most interestingly, the catalyst can be recycled several times without significantly affecting the rates of the hydrolysis reaction. In addition to being a very good catalyst for phosphate ester hydrolysis, the heterogeneous catalyst **15** was also found to be an excellent reagent for modifying plasmid DNA.¹⁴

The strength of the above methodology is that it is amenable to polymer ligand engineering and allows the preparation of a number of polymer-based ligands. Accordingly, we incorporated phosphines instead of pyrazolyl groups as coordinating groups. The resulting multiphosphine polymeric ligand (**19**) is effectively metalated by Pd(0) to afford (**20**) (Chart 1).¹⁵ The latter is a robust heterogeneous catalyst for the Heck arylation reaction (Scheme 1). Another attractive feature is that because of the cross-linked polymer support, palladium leaching is minimal. Consequently **20** can be recycled several times for the catalytic reaction without any significant reduction in activity.¹⁵

Following the successful utilization of the pyrazolylcyclophosphazenes, it was of interest to see whether other P–N ligands can be built using cyclophosphazene supports. *N*-Methylhydrazine regioselectively reacted with chlorocyclophosphazenes to afford $N_3P_3[N(Me)NH_2]_6$ (**21**), $N_3P_3(OPh)[N(Me)NH_2]_5$ (**22**), *gem*- $N_3P_3Ph_2[N(Me)NH_2]_4$ (**23**), *gem*- $N_3P_3(O_2C_{12}H_8)[N(Me)NH_2]_4$ (**24**), and $N_3P_3(OPh)_5[N(Me)NH_2]$ (**25**) (Chart 3).¹⁶

CHART 1. Metalated Multisite Coordination Polymers

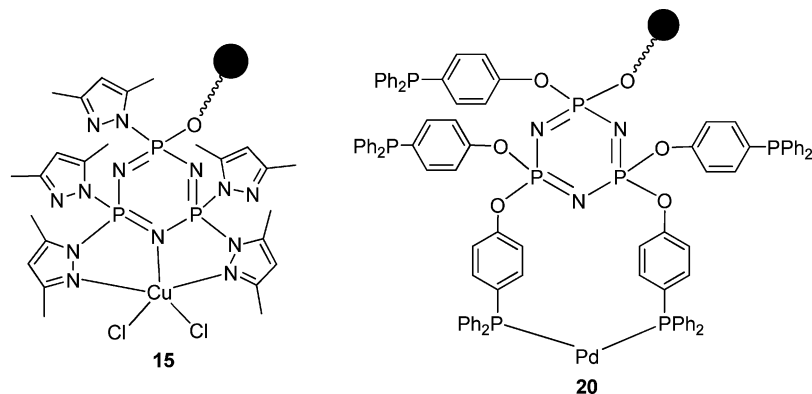
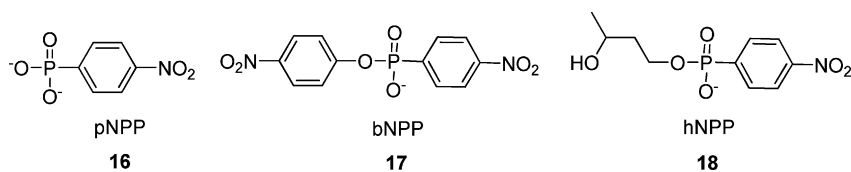
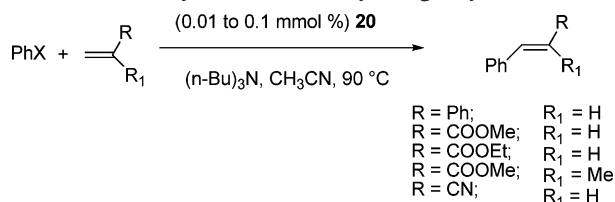


CHART 2. Substrates Used in Phosphate Ester Hydrolysis



SCHEME 1. Heck Arylation Reaction by Using Polymer 20



Importantly, nucleophilic substitution chemistry of cyclophosphazenes allows the placement of the desired number of hydrazide arms, as well as control of their stereochemistry. Further, all of these cyclophosphazene hydrazides possess reactive terminal -NH₂ groups, which were utilized to prepare a number of cyclophosphazene-supported multiferrocene assemblies by condensation with ferrocene-2-carboxaldehyde (**26**, **27**) (Chart 3).¹⁶ X-ray crystal structure of the hexaferrocene compound N₃P₃[N(Me)N=CH-C₅H₄FeC₅H₅]₆ (**26**) reveals that the cyclophosphazene platform conveniently supports the six ferrocene arms, the latter being symmetrically disposed, three on each side of the planar cyclophosphazene ring. Cyclic and differential pulse voltammetric studies on these ferrocene assemblies reveal that a single, essentially reversible oxidation peak is observed indicating that all the pendant ferrocene moieties present in these compounds are oxidized at the same potential.¹⁶ This behavior is similar to what we observed for stannoxane-supported multiferrocene assemblies.¹⁷

Cyclophosphazene hydrazides can also be utilized as multisite coordination ligands. Thus, the tetrahydrazide *spiro*-N₃P₃(O₂C₁₂H₈)[N(Me)NH₂]₄ (**23**) reacts with metal salts to afford 2:1 complexes (**28**–**31**) (Chart 4). In these compounds each

of the cyclophosphazene ligands functions as a *nongeminal* N₃ donor (Chart 4).¹⁸ It is of interest to note that even hydrated metal salts can react with the cyclophosphazene hydrazides without causing P–N bond hydrolysis. This is in contrast to the hydrolytic sensitivity of the pyrazolyl cyclophosphazenes noted above.

Cyclophosphazene hydrazides can be elaborated into more complex coordinating platforms (**32**) by condensation with salicylaldehyde.¹⁹ The tetrahydrazone (**32**), thus obtained, has on either side two imino nitrogen atoms and two phenolate oxygen atoms providing two pockets of coordination suitable for binding two metal ions. In accordance with this expectation, the reaction of **32** with Cu(OAc)₂·H₂O or CuCl₂ in presence of sodium hydride leads to a dinuclear compound, which dimerizes in the solid state affording a tetranuclear compound (**33**) containing a central Cu₂O₂ ring (Scheme 2).¹⁹ Remarkably, the formation of the latter is accompanied by the formation of 15 contiguous rings.¹⁹

II.2. Pyridyloxy Cyclophosphazenes. Both pyrazolyl cyclophosphazenes and cyclophosphazene hydrazides described above are *rigid* ligands. Coordination of the pyrazolyl arms (in conjunction with the cyclophosphazene ring nitrogen atom) leads to the generation of five-membered rings. The flexibility of the cyclophosphazene coordination platform can be considerably enhanced by incorporating a hinge atom that serves as a spacer between the coordinating arm and the cyclophosphazene support. This idea was exploited by Brodie et al. and us in the design of pyridyloxy cyclophosphazenes.^{20–22} We have found that hexakis(2-py-

CHART 3. Cyclophosphazene Hydrazides and Hydrazones

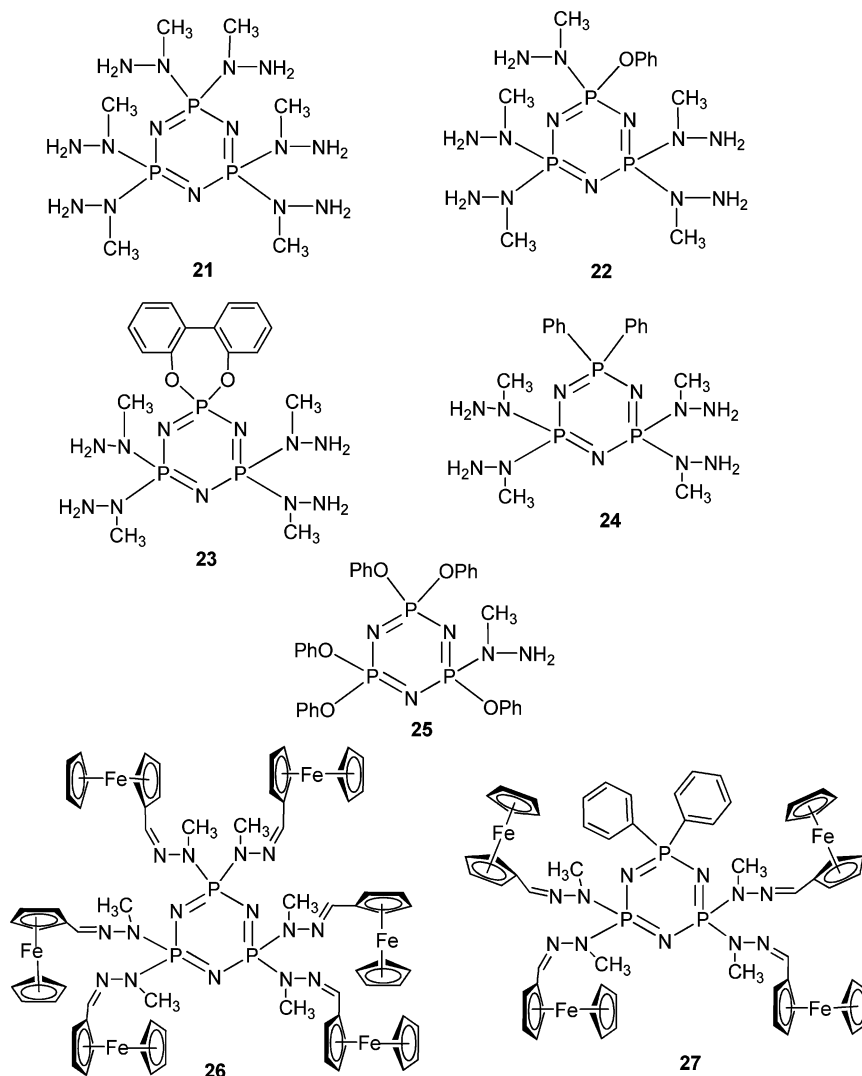
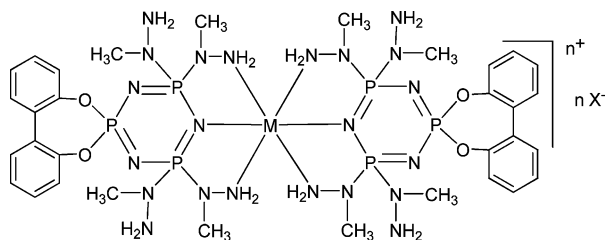


CHART 4. Metal Complexes of Cyclophosphazene Hydrazides



M = Ni; X = NO₃⁻; n = 2 (**28**) M = Cd; X = NO₃⁻; n = 2 (**30**)

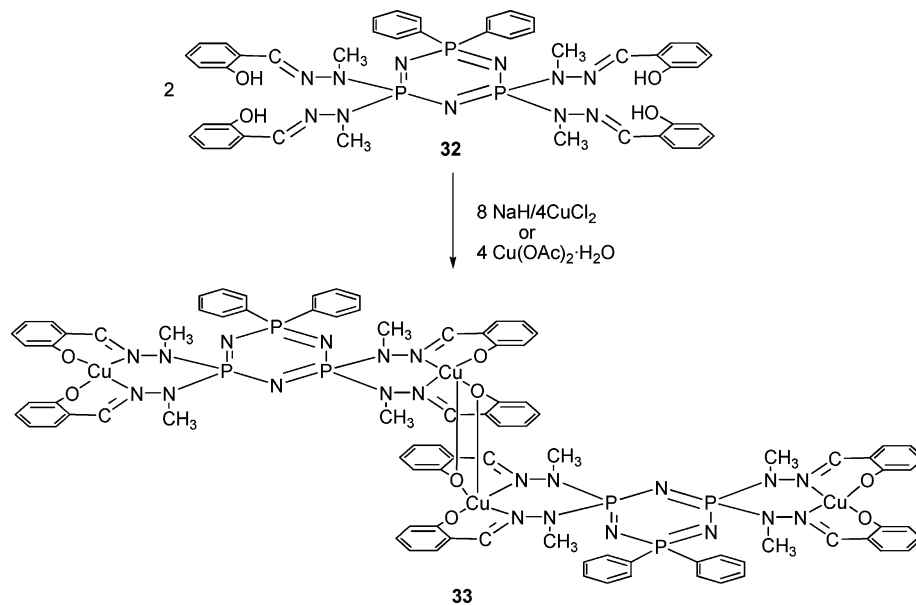
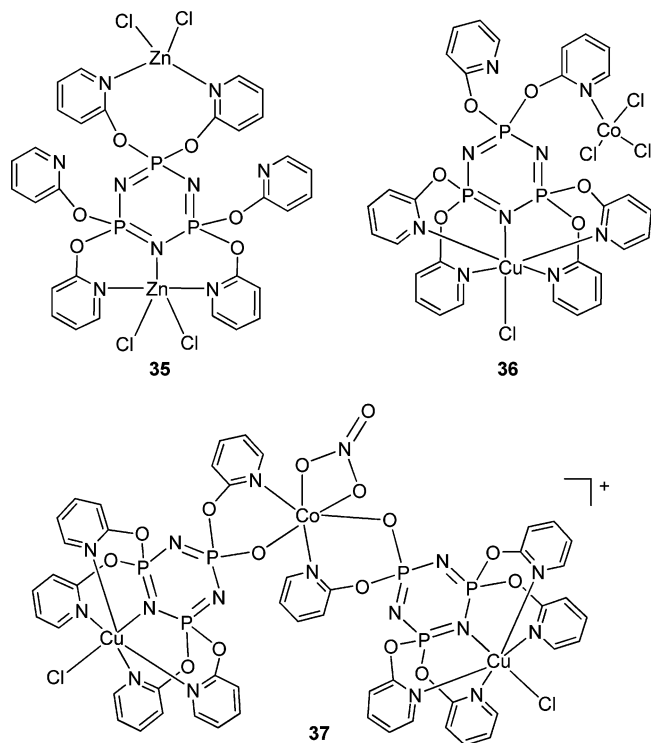
M = Zn; X = NO₃⁻; n = 2 (**29**) M = Co; X = Cl⁻; n = 3 (**31**)

ridyloxy)cyclophosphazene **34** binds with transition metal ions to afford dinuclear complexes.²⁰ In these complexes, the flexible ligand periphery efficiently binds to the metal ions using a variety of coordination modes. For example, with Zn(II) a homodinuclear complex (**35**) is formed (Chart 5).²⁰ On the other hand, in the heterodinuclear complex **36**, while the cobalt ion is bound only by one of the pyridyloxy arms,

the copper ion is bound by four pyridyloxy groups and one ring nitrogen atom.²⁰ In an interesting reaction, **34** upon treatment with CuCl₂ followed by Co(NO₃)₂ · 6H₂O afforded a trinuclear heterobimetallic complex (**37**) (Chart 5).²⁰ The formation of this compound involves an unusual P–O bond cleavage involving one of the phosphorus–pyridyloxy bonds. A central six-coordinate cobalt can be viewed as bridging two copper-metalated cyclophosphazene rings.²⁰ Recently, dicopper derivatives of pyridyloxy cyclotetraphosphazenes have been prepared. In some of these systems, the two copper atoms separated by the phosphazene unit experience antiferromagnetic coupling.²¹

The nuclearity of the metal complexes can be modulated by ligand design. The reaction of N₃P₃(O₂C₁₂H₈)(OC₅H₄-2-N)₄ (**38**) with metal salts leads to exclusive formation of mononuclear complexes (**39–41**) (Scheme 3).²²

SCHEME 2. Tetranuclear Copper Assembly

CHART 5. Metal Complexes of **34**

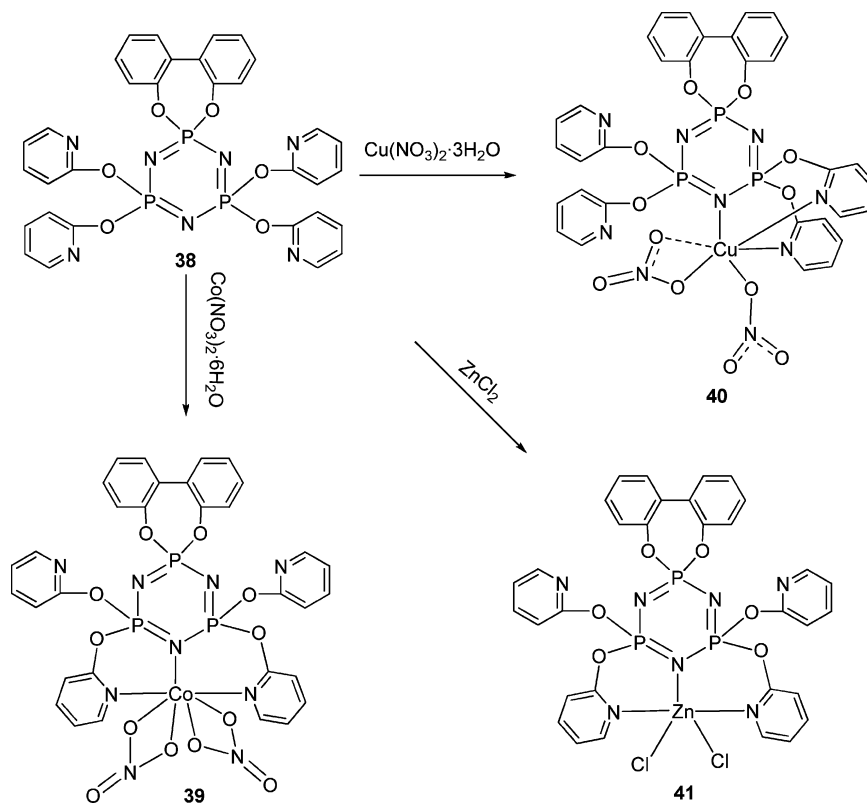
In addition to the ligands described here, an important contribution to cyclophosphazene ligands is the deprotonation methodology developed by Steiner and co-workers for building multimetallic architectures.²³

II.3. Carbophosphazene-Based Ligands. Unlike cyclophosphazenes, heterocyclophosphazenes such as cyclocarbophosphazenes have been much less studied. Utilizing $[\{\text{NP}(\text{Cl})_2\}\{\text{NC}(\text{Cl})_2\}]$ (**42**) as the precursor, we prepared $[\{\text{NP}(3,5-$

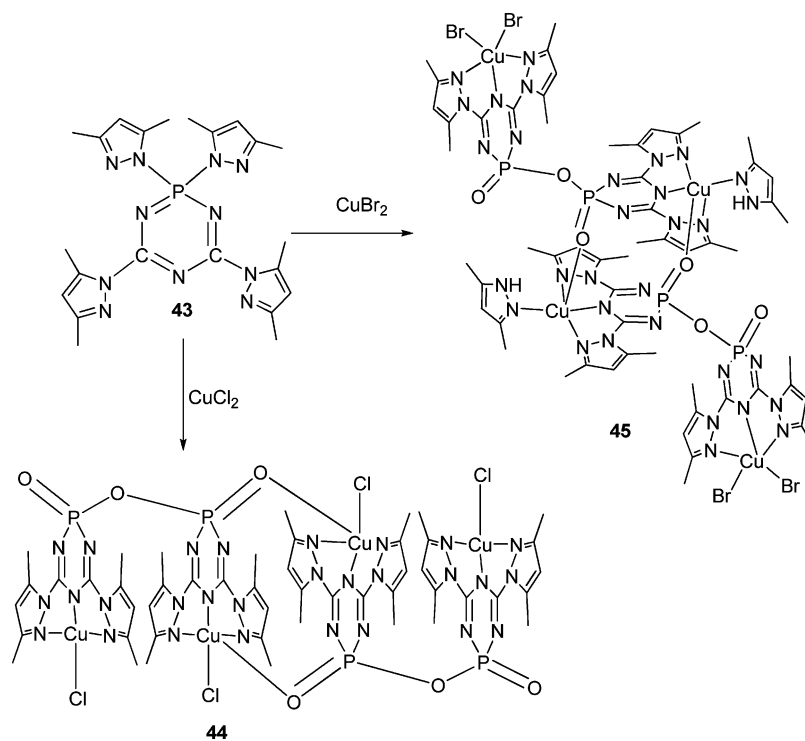
$\text{Me}_2\text{Pz})_2\}\{\text{NC}(3,5-\text{Me}_2\text{Pz})_2\}]$ (**43**). The experience of pyrazolyl cyclophosphazenes suggested to us that the P–N bonds in $[\{\text{NP}(3,5-\text{Me}_2\text{Pz})_2\}\{\text{NC}(3,5-\text{Me}_2\text{Pz})_2\}]$ (**43**) would be prone to hydrolysis upon metalation while the C–N bonds would be more robust.²⁴ This expectation was realized in the reaction of **43** with CuX_2 ($\text{X} = \text{Cl}, \text{Br}$), which afforded novel examples of cyclocarbophosphazene-containing tetramers $[\{\text{N}_3\text{C}_2(3,5-\text{Me}_2\text{Pz})_2\text{P}(\text{O}) \cdot \text{CuCl}_2\text{O}\}]_2$ (**44**) and $[\{\text{N}_3\text{C}_2(3,5-\text{Me}_2\text{Pz})_2\text{P}(\text{O}) \cdot \text{CuBr}_2\text{O}\}\{\text{N}_3\text{C}_2(3,5-\text{Me}_2\text{Pz})_2\text{P}(\text{O}) \cdot \text{Cu}(3,5-\text{Me}_2\text{PzH})\}]_2$ (**45**) (Scheme 4). Interestingly these tetramers are held together by P–O–P and P–O–Cu linkages. Importantly, the formation of the tetrameric assemblies is driven by an in situ P–N bond cleavage. The reaction intermediates containing P–OH groups condense to generate the P–O–P linkages.²⁴ It is to be noted that during this process the C–N bonds remain intact. The coordination arms attached to the carbon centers hold the metal assembly together.

III. Acyclic Phosphorus Systems

III.1. Phosphorus Pyrazolides. The prospect of a phosphorus atom acting as a support to hold multiple pyrazolyl arms is quite interesting. In contrast to boron, the advantage with phosphorus is the tunability of the oxidation state, as well as the ease of changing the number of pyrazolyl arms. Accordingly, we prepared $\text{MeP}(\text{S})(3,5-\text{Me}_2\text{Pz})_2$ (**46**) and studied its reaction with CuCl_2 . To our surprise, we have observed that in presence of slight traces of adventitious moisture, the reaction affords a tetranuclear copper phosphonate (**47**) (Scheme 5).²⁵ The structure of the latter showed that it is made up of

SCHEME 3. Monometallic Derivatives of **38**

SCHEME 4. Tetranuclear Assemblies Obtained by P–N Hydrolysis



two dinuclear copper cores, which are bridged to each other by two capping tridentate phosphonate ligands. The mechanism of this reaction was probed, and this revealed that the

parent ligand itself is quite stable to hydrolysis. Upon metalation the electrophilicity of the phosphorus center is accentuated, which leads to desulfurization and P–N bond

SCHEME 5. Tetracopper Assembly Obtained by Hydrolysis of 46

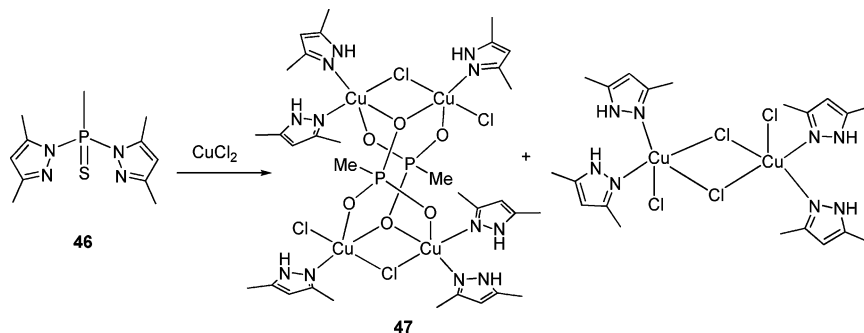
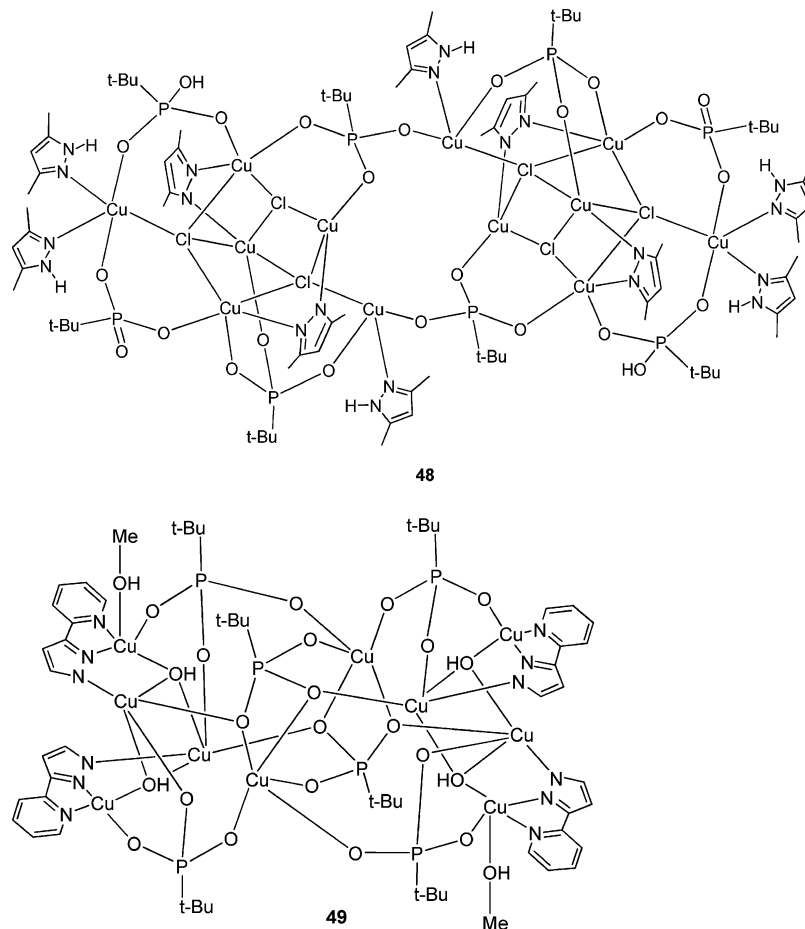


CHART 6. Multicopper Assemblies Prepared by Using Phosphonate and Pyrazole Ligands

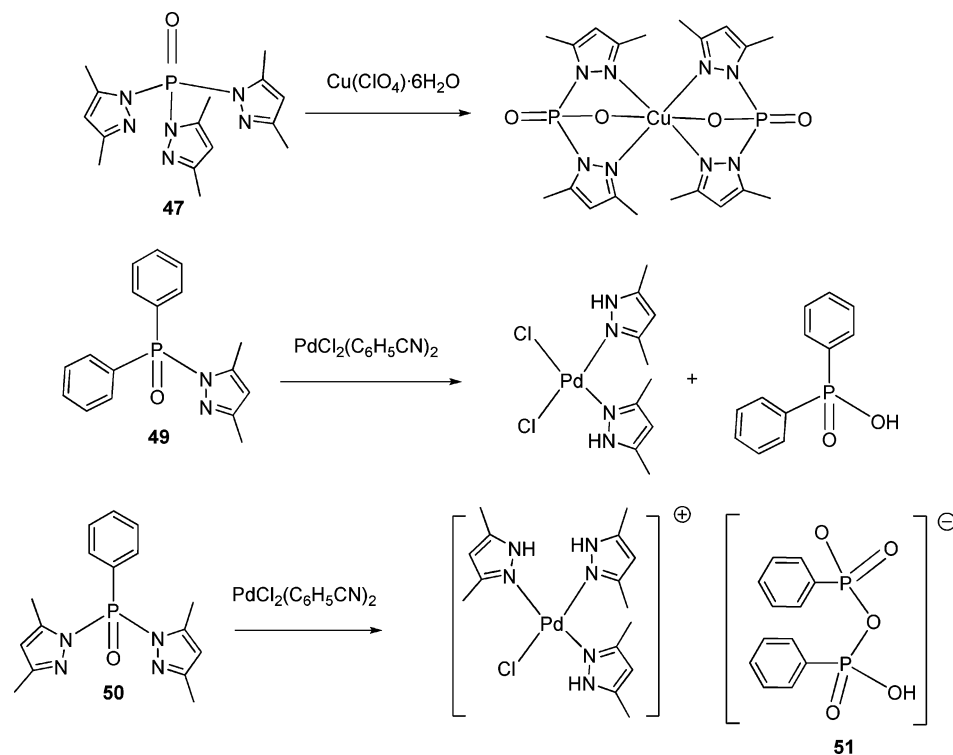


cleavage. The in situ generated phosphonic acid and pyrazole ligands assist the formation of the tetranuclear assembly.²⁵ Based on this inference, we have shown that the *direct* reaction of a phosphonic acid with transition metal salts in presence of ancillary nitrogen-containing ligands such as pyrazole leads to the formation of a variety of multinuclear molecular transition metal phosphonates, representative examples (**48**, **49**) of which are shown in Chart 6.²⁶ However, this aspect will not be covered in this Account.

Metal-induced P–N bond hydrolysis of phosphorus pyrazolides is also found with $P(O)(3,5-Me_2Pz)_3$ (**47**),²⁷ $[(SP(2-pypz)_3]$ (**48**),²⁸ $Ph_2P(O)(3,5-Me_2Pz)$ (**49**),²⁹ and $PhP(O)(3,5-Me_2Pz)_2$ (**50**).²⁹ For example, interaction of the latter with $PdCl_2$ generates $[Pd(3,5-Me_2Pz)_3Cl]^+[PhP(O)(OH)OP(O)_2Ph]^-$ (**51**) (Scheme 6).²⁹

III.2. Phosphorus-Supported Hydrazones. Phosphorus hydrazides such as $(S)P[N(Me)NH_2]_3$ (**52**) and $PhP(O)[N(Me)NH_2]_2$ (**53**) have been utilized by Majoral and co-workers for the preparation of macrocycles and cryptands.³⁰ The coor-

SCHEME 6. Hydrolysis of Phosphorus Pyrazolides upon Interaction with Transition Metal Ions



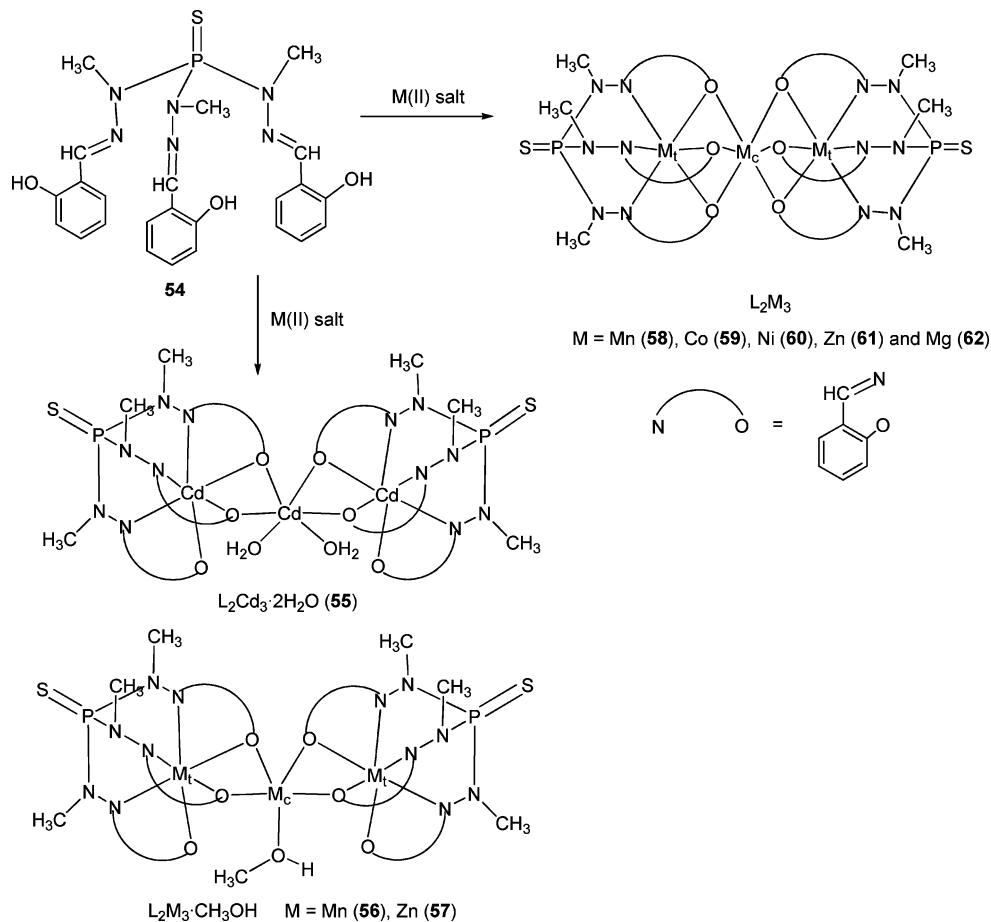
dination chemistry of these compounds has received some attention.³¹ We felt that the versatility of these systems can be greatly enhanced by elaborating them into hydrazones. Accordingly, we assembled the multisite coordination ligand $\text{P}(\text{S})[\text{N}(\text{Me})\text{N}=\text{CH}-\text{C}_6\text{H}_4-2\text{-OH}]_3$ (LH_3) (**54**) from the condensation of $(\text{S})\text{P}[\text{N}(\text{Me})\text{NH}_2]_3$ and *o*-hydroxybenzaldehyde.³² LH_3 has three imino nitrogen atoms and three acidic phenolic oxygen atoms as potential coordinating sites. Remarkably, the reaction of LH_3 with a number of first row divalent transition metal salts afforded homometallic trinuclear complexes in almost quantitative yields (Scheme 7).^{32–34} In all cases, the two terminal metal centers are encapsulated by a facial 3N,3O coordination environment. In many cases, the central metal ion has a 6O coordination environment (Scheme 7). The presence of solvent molecules changes the nature of coordination of the central metal atom in some instances [$\text{L}_2\text{Cd}_3 \cdot 2\text{H}_2\text{O}$ (**55**); $\text{L}_2\text{Mn}_3 \cdot \text{MeOH}$ (**56**), and $\text{L}_2\text{Zn}_3 \cdot \text{MeOH}$ (**57**); Scheme 7].³⁴ Perfectly linear arrangement of the metal atoms in these L_2M_3 trinuclear compounds [$\text{M} = \text{Mn}$ (**58**), Co (**59**), Ni (**60**), Zn (**61**), Mg (**62**)] gives rise to a paddle-wheel-type architecture when viewed from one end of the molecule.^{32,33}

An interesting aspect of the stereochemistry of the trinuclear complexes is that although the ligand is achiral, coordination with metal ion induces chirality in the complexes. The three chelate rings formed upon complexation can have $\lambda\lambda\lambda$ (all the rings oriented in the same direction, clockwise with

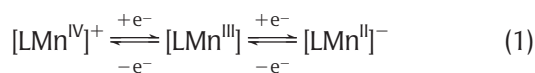
respect to intermetal axis) or $\delta\delta\delta$ orientations (all rings oriented in the same direction, anticlockwise with respect to intermetal axis). In $\text{L}_2\text{Cd}_3 \cdot 2\text{H}_2\text{O}$ (**55**), $\text{L}_2\text{Mn}_3 \cdot \text{MeOH}$ (**56**), $\text{L}_2\text{Zn}_3 \cdot \text{MeOH}$ (**57**), L_2Co_3 (**59**), L_2Ni_3 (**60**), and L_2Zn_3 (**61**), the orientation of the three chelating rings in the front and back side of the complex are the same; that is, these compounds exist as pure enantiomers in their molecular structures. In L_2Mn_3 (**58**) and L_2Mg_3 (**62**), the orientations in the front and back are opposite, that is, these exist in the meso forms. Interestingly the $\text{M}_t-\text{M}_c-\text{M}_t$ bond angles are a perfect 180° for the meso forms. In other instances, these bond angles are always slightly less than 180° . The crystal structures of $\text{L}_2\text{Cd}_3 \cdot 2\text{H}_2\text{O}$ (**55**), $\text{L}_2\text{Mn}_3 \cdot \text{MeOH}$ (**56**), and $\text{L}_2\text{Zn}_3 \cdot \text{MeOH}$ (**57**) reveal the presence of chiral recognition in their supramolecular structures corresponding to the interaction of molecules with a $\Lambda-\Lambda$ configuration with those having $\Delta-\Delta$ configuration. These $\text{C}-\text{H} \cdots \text{S}=\text{P}$ intermolecular interactions afford a zig-zag one-dimensional double-bridged polymer chain.³⁴

Among the various trinuclear complexes, $\text{L}_2\text{Cd}_3 \cdot 2\text{H}_2\text{O}$ (**55**) and L_2Mg_3 (**62**) show emission in the solid-state, solution, doped polymer, and thin films (Figure 1). The luminescent properties observed in the solid state (emission at $\lambda = 448$ nm for L_2Mg_3 and 493 nm for $\text{L}_2\text{Cd}_3 \cdot 2\text{H}_2\text{O}$) is very similar to that found in dichloromethane solution ($\lambda = 442$ nm for L_2Mg_3 and 458 nm for $\text{L}_2\text{Cd}_3 \cdot 2\text{H}_2\text{O}$).^{33,34}

SCHEME 7. Synthesis of Trinuclear Metal Assemblies



In contrast to the trinuclear complexes formed in the reactions of LH_3 with divalent metal salts, exclusive mononuclear complexes LM [$M = \text{Sc (63), Cr (64), Mn (65), Fe (66), Co (67), and Ga (68)}$] are formed in its reaction with trivalent metal salts.³⁵ All three phenolate oxygen atoms of a given ligand along with the three imino nitrogen atoms encapsulate the trivalent metal ion in a facial $3N,3O$ coordination environment. Both LMn (65) and LFe (66) are high-spin complexes. The electrochemical behavior of LMn (65) (eq 1; Figure 2) reveals that the complex is reversibly reduced as well as oxidized by a single-electron process suggesting that the hexadentate $[L]^{3-}$ ligand stabilizes manganese in oxidation states ranging from +2 to +4.³⁵



The strategy utilized for the preparation of LH_3 has the merit that it is easily adaptable for other types of ligands. As a test of this concept, we condensed 4(5)-imidazole carboxaldehyde with $(S)P[N(\text{Me})NH_2]_3$. The in situ generated ligand containing three imidazole arms, $[(S)P[N(\text{Me})N=CH\text{Im}]_3$ (69), was allowed to react with metal salts to afford mononuclear complexes $[L \cdot M][NO_3]_2$ [$M = \text{Co (70); Cd (71)}$] and $[L \cdot M][ClO_4]_2$ [$M = \text{Ni (72)}$].³⁶ The molec-

ular structures of the mononuclear complexes are quite similar and consist of the metal ion being encapsulated by the neutral hexadentate ligand. The metal ion is present in a distorted trigonal prismatic coordination environment. The $Zn(II)$ complex presented an interesting situation (Scheme 8). One full molecule of a dicationic mononuclear $Zn(II)$ complex (73) and half of a tetracationic 20-membered $Zn(II)$ metallamacrocycle (74) were present in its asymmetric unit along with four nitrate anions (see Figure 3 for the structure of the macrocycle). Such a coexistence/cocrystallization of metal complexes possessing different compositions (structures) in the same unit cell of a crystalline lattice, if not unprecedented, is certainly very rare. Solution studies using ^{31}P NMR and ESI-MS revealed that in solution also both the macrocycle and the mononuclear structures exist and are perhaps present in a dynamic equilibrium.³⁶

IV. 3d–4f Assemblies: New Single-Molecule Magnets

The spontaneous organization of linear trimetallic assemblies using phosphorus-supported tris hydrazone ligands can be advantageously fine-tuned by subtle variations on the ar-

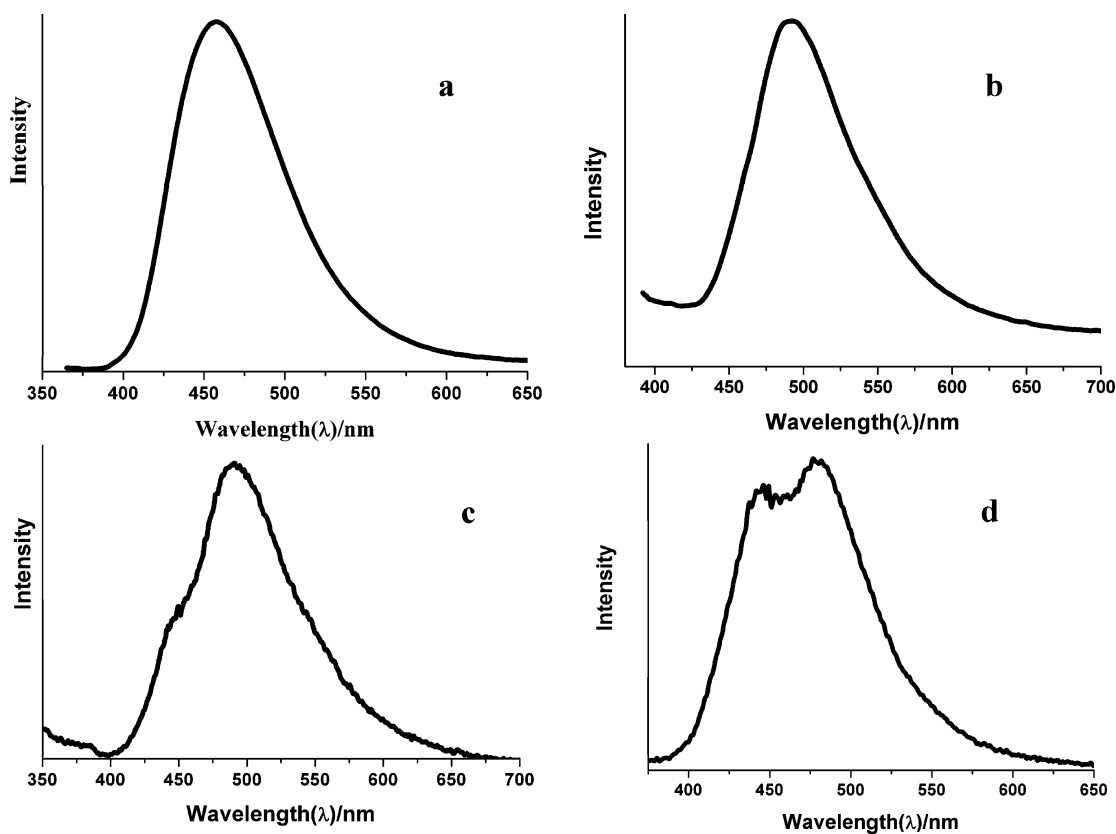


FIGURE 1. Emission spectra of L_2Cd_3 complex in (a) solution, (b) solid state, (c) thin film, and (d) doped polymer. Reproduced with permission from ref 34. Copyright 2005 American Chemical Society.

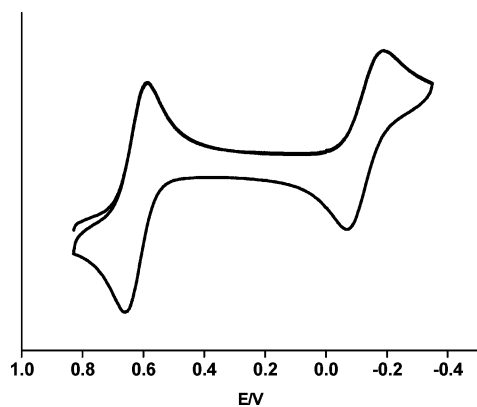
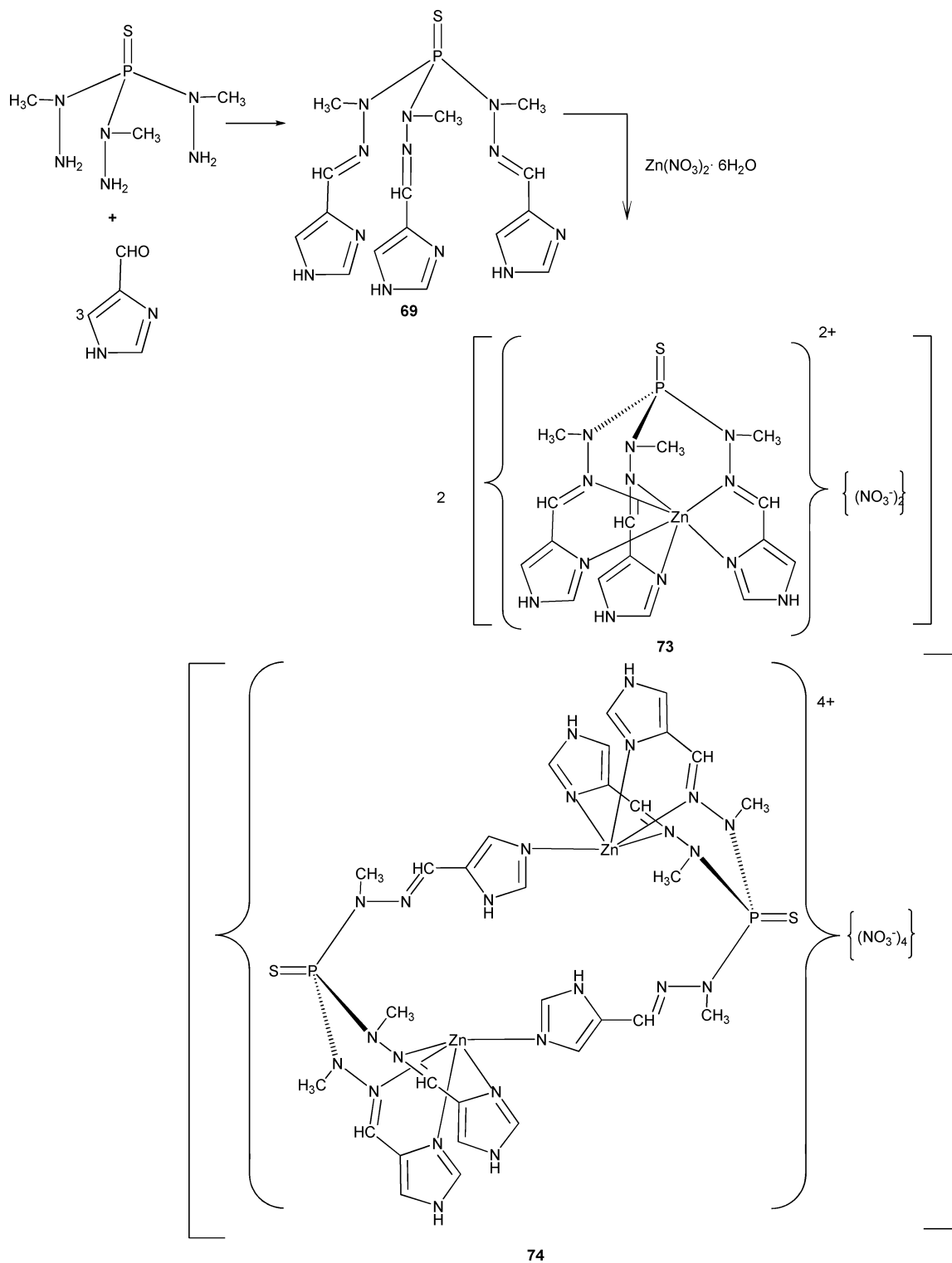


FIGURE 2. Cyclic voltammogram of LMn in CH_2Cl_2 recorded against Ag/AgCl. Scan rate 100 mV S^{-1} . Reproduced with permission from ref 35. Copyright 2008 Wiley.

matic substituents. We were intrigued by the possibility of generating new magnetic materials in general and single-molecule magnets in particular by using the family of ligand systems described in this Account. This was motivated by the recent interest in molecular magnetism in general and in superparamagnetism and single-molecule magnets (SMMs) in particular.^{37,38} SMMs, once magnetized, retain their magnetization (or undergo a slow relaxation of magnetization) below certain temperatures, even after the field is switched off. The criteria for SMM behavior appear to be the presence of a large

ground state spin (S) and a large uniaxial magnetic anisotropy (large negative D and small E considering the following Hamiltonian anisotropy term: $H = DS_{T_z}^2 + E(S_{T_x}^2 - S_{T_y}^2)$). The potential applications of SMMs (in diverse fields ranging from data storage to quantum computing) coupled with the interesting physics associated with them has prompted many chemists to prepare a wide range of complexes so that they can be studied thoroughly in terms of their magnetic behavior.^{37,38} The discovery that the mixed valent dodecanuclear manganese cluster $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ (**75**) (ground state $S = 10$) containing Mn^{3+} and Mn^{4+} sites is a SMM at low temperatures³⁹ has prompted the examination of many polynuclear metal complexes.³⁸ More recently some lanthanide complexes as well as some mixed 3d–4f complexes have also been shown to behave as SMMs.^{40,41} The latter are a new paradigm in this area involving magnetic interactions between a lanthanide and a transition metal ion. Traditionally, in all the systems that have been examined the lanthanide metal ion was chosen with an intention of bringing about magnetic anisotropy. This design naturally excluded Gd(III) since by possessing a half-filled 4f shell it is usually considered as an isotropic magnetic center with a quenched orbital contribution. However, we decided to look at this

SCHEME 8. Mononuclear **73** and Macrocyclic Zn(II) (**74**) Compounds Formed from **69**

choice from a different perspective. The fact that the ground state spin of Gd(III) ($S = 7/2$) is very high can be looked upon as an advantage to generate high-spin complexes. In order to bring anisotropy to the system, we decided on using the highly anisotropic Co(II) ions. Such a strategy of bringing

together an anisotropic Co(II) and a high-spin Gd(III) has never been attempted hitherto. An appropriate ligand design for forming the Co–Gd assembly was formulated to include more coordination sites than those offered by LH₃. In keeping with this reasoning, we modified LH₃ and prepared L'H₃ (**76**) by the

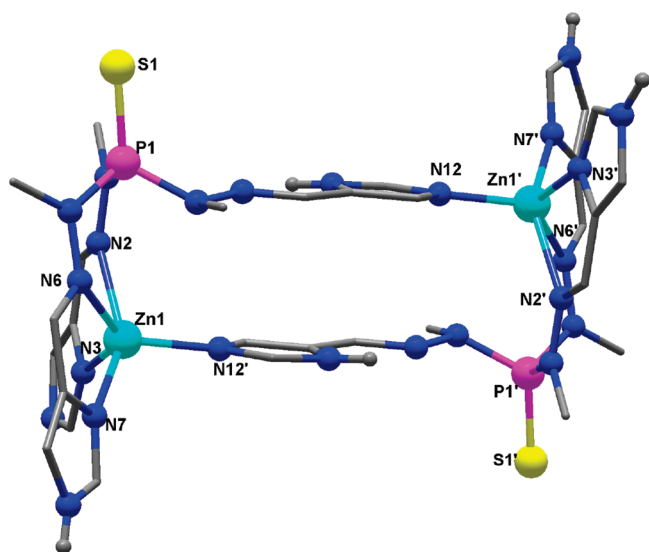


FIGURE 3. Structure of the macrocycle **74**. Reproduced with permission from ref 36. Reproduced by permission of The Royal Society of Chemistry (RSC).

condensation of *o*-vanillin with (S)P[N(Me)NH₂]₃.^{42–45} L'H₃ (**76**) contains nine potential coordination sites: three imino nitrogen atoms, three phenolate oxygen atoms, and three methoxy oxygen atoms. The latter, although weakly binding to

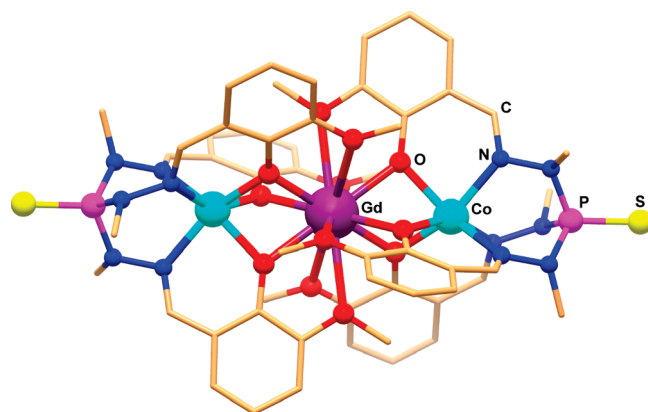
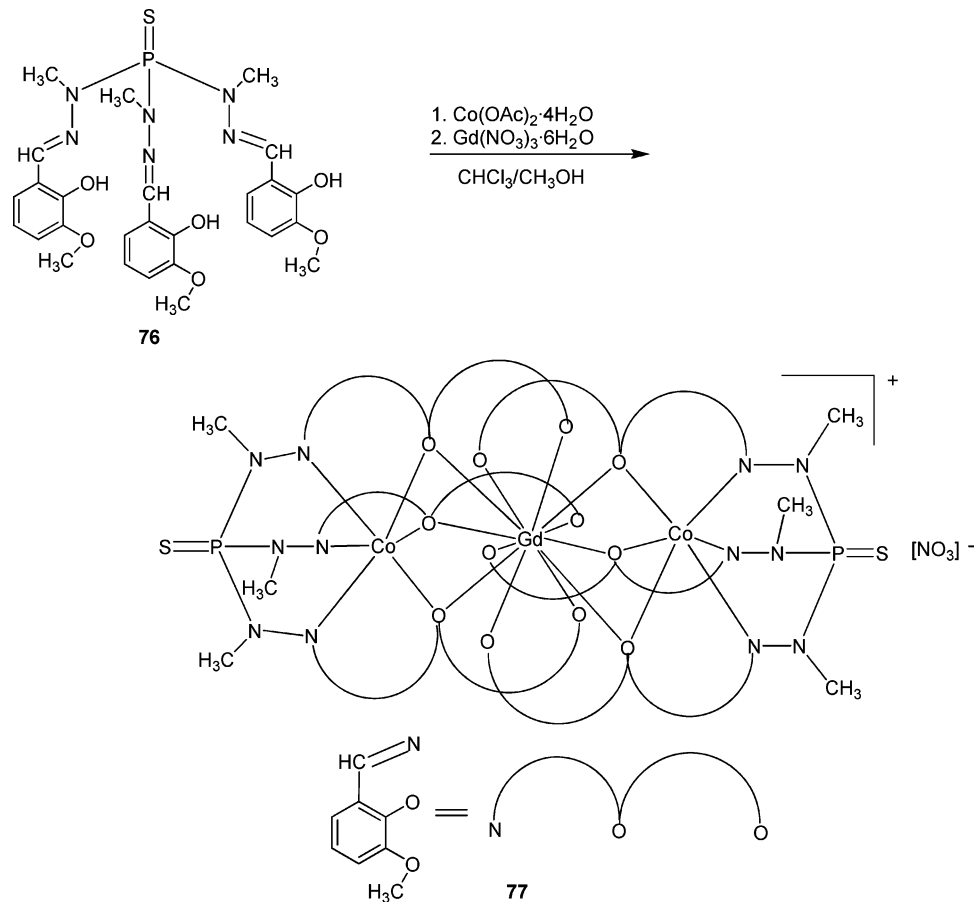


FIGURE 4. Structure of the cationic portion, [L₂Co₂Gd]⁺, of **77**. Reproduced with permission from ref 42. Copyright 2007 American Chemical Society.

transition metal ions, have good affinity for lanthanide ions. Accordingly, L'H₃ (**76**) was first reacted with Co(O₂CCH₃)₂ · 4H₂O salt followed by Gd(NO₃)₃ · 6H₂O to give [L₂Co₂Gd][NO₃] (**77**) (Scheme 9). Eighteen coordination sites of the two ligands are completely utilized to hold the three metal ions together (Figure 4). The two cobalt ions present in this trimetallic complex are six-coordinate in a distorted octahedral geometry (3N,3O coordination) (Figure 4). The central gadolinium ion

SCHEME 9. Synthesis of **77**, [L₂Co₂Gd][NO₃]



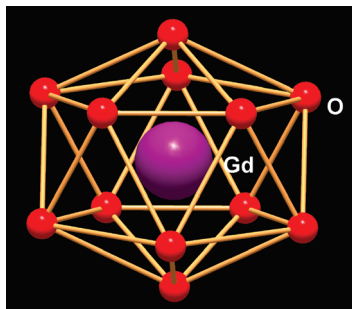


FIGURE 5. Distorted icosahedral arrangement around Gd^{III} in **77**. Reproduced with permission from ref 42. Copyright 2007 American Chemical Society.

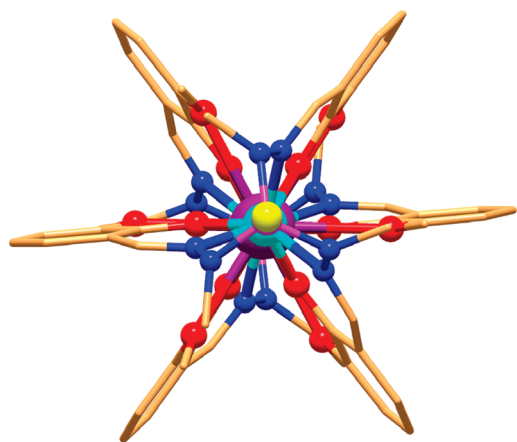


FIGURE 6. Paddle wheel arrangement of [L₂Co₂Gd]⁺ in **77**. Reproduced with permission from ref 42. Copyright 2007 American Chemical Society.

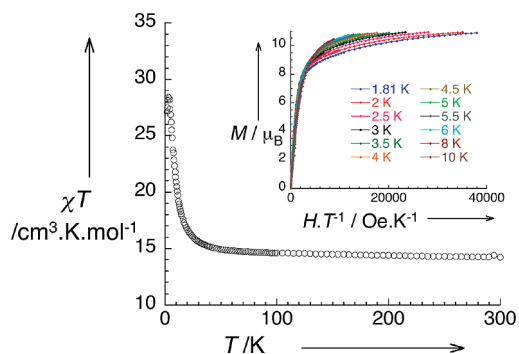


FIGURE 7. Temperature dependence of χT (where $\chi = M/H$) at 1000 Oe for complex **77**. Inset shows a plot of magnetization vs H/T between 1.8 and 10 K. Reproduced with permission from ref 42. Copyright 2007 American Chemical Society.

has a coordination number of 12 (12O, six phenolate and six methoxy oxygens) in a distorted icosahedral geometry (Figure 5). Thus, the Gd(III) and Co(II) centers are connected to each other by means of three bridging phenolate oxygen atoms, which generate three four-membered GdCoO₂ rings (Figure 4). The Co–Gd–Co array is perfectly linear, and the whole complex has a paddle-wheel architecture when viewed from one end of the molecule (Figure 6). While the Co–Gd

distance is 3.307(1) Å, the inter-Co–Co distance is 6.614(2) Å. The end–end distance of the cationic complex (between the two terminal sulfur atoms) is 17.120(5) Å.⁴²

Detailed magnetic studies on the cationic complex established that it is a new SMM. The plot of χT vs T indicates a continuous increase until a final maximum is reached at 28.5 cm³·K·mol⁻¹ (Figure 7). After this temperature, the χT value decreases presumably because of magnetic anisotropy/weak antiferromagnetic interactions. Field dependence of magnetization revealed no true saturation even at 7 T and 1.81 K (inset of Figure 7) indicating that significant anisotropy prevents saturation. This is also confirmed by the observation that the data do not superimpose on a single master curve (inset of Figure 7). Although no significant hysteresis was observed in the M vs H plot, SMM behavior was confirmed by ac susceptibility measurements, which showed nonzero χ'' values (Figure 8). A slow relaxation of the magnetization was clearly inferred, and it was possible to estimate the relaxation time. From an Arrhenius-type plot (Figure 9), the energy gap for the SMM, Δ , was estimated to be 27.2 K, while the pre-exponential factor τ_0 was obtained as 1.7×10^{-7} s. In order to establish whether quantum tunneling has a significant role in the relaxation of the magnetization, the frequency dependence of the ac susceptibility was measured at 3.8 K under the influence of small DC fields. The latter removes the degeneracy of $\pm m_s$ states and therefore allows measurement of relaxation time of the nonquantum tunneling processes. The near invariance of the τ_0 values at zero and 1000 Oe field gives a good indication that the relaxation of magnetization occurs predominantly through nonquantum tunneling pathways.⁴² The synthetic strategy used for Co₂Gd complexes has been successfully extended to other Co₂Ln complexes (Ln = Eu, Tb, Dy, Ho).⁴³

The synthetic strategy used for preparing the heterometallic linear trinuclear 3d–4f complexes using L'H₃ is entirely general. To demonstrate this, we prepared the full range of complexes [L'₂Ni₂Ln][ClO₄] (Ln = La (**78**), Ce (**79**), Pr (**80**), Nd (**81**), Sm (**82**), Eu (**83**), Gd (**84**), Tb (**85**), Dy (**86**), Ho (**87**), and Er (**88**)). All of these complexes are isostructural with the Co₂Gd complex described above. The Ni–Ni separations in these complexes range from 6.84 to 6.48 Å. The phenomenon of lanthanide contraction is demonstrated quite elegantly in the variation of the metric parameters. Thus, the Ni–Ni, Ni–Ln, and Ln–O_{phenolate} bond distances in these complexes show a gradual reduction proceeding from **78** to **88** (Table 1; Figure 10).⁴⁴

The importance of Co(II) for the SMM behavior of the Co₂Gd complex is indicated when it is replaced by Ni(II). Thus, the analogous Ni₂Gd complex does not show SMM

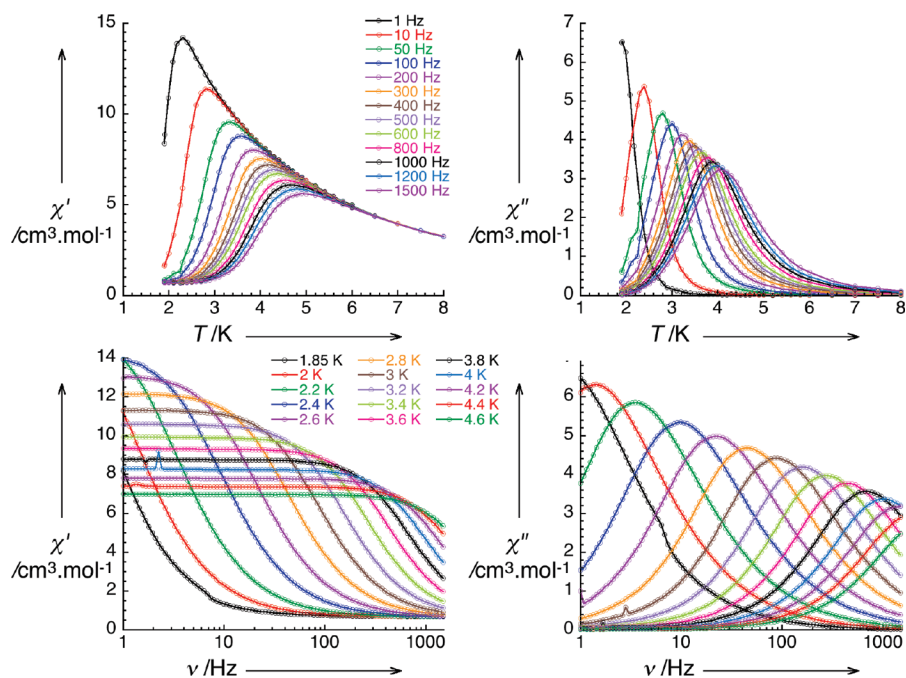


FIGURE 8. Temperature (top) and frequency (bottom) dependence of the in-phase and out-of-phase ac susceptibility at different frequencies and different temperatures under zero dc field. Reproduced with permission from ref 42. Copyright 2007 American Chemical Society.

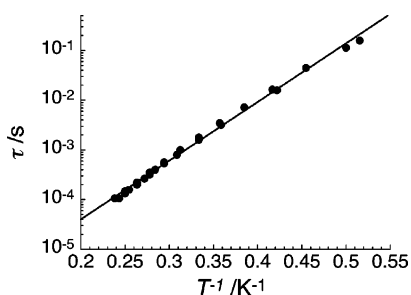


FIGURE 9. τ vs T^{-1} plot at $H_{dc} = 0$. The solid lines represent an Arrhenius fit of the data. Reproduced with permission from ref 42. Copyright 2007 American Chemical Society.

TABLE 1. Important Bond Distances (Å) for **78–88**

	Ni–Ni	Ni–Ln	Ln–O _{phenolate}
Ni ₂ La (78)	6.8409(11)	3.4209(7)	2.538(5)
Ni ₂ Ce (79)	6.7942(9)	3.3973(5)	2.513(4)
Ni ₂ Pr (80)	6.7617(16)	3.3811(9)	2.495(4)
Ni ₂ Nd (81)	6.7337(10)	3.3673(7)	2.482(4)
Ni ₂ Sm (82)	6.6679(11)	3.3345(7)	2.450(5)
Ni ₂ Eu (83)	6.6449(9)	3.3230(6)	2.435(4)
Ni ₂ Gd (84)	6.6268(19)	3.3142(10)	2.423(4)
Ni ₂ Tb (85)	6.5952(9)	3.2976(6)	2.409(4)
Ni ₂ Dy (86)	6.5570(8)	3.2795(5)	2.392(4)
Ni ₂ Ho (87)	6.5056(10)	3.254(6)	2.377(4)
Ni ₂ Er (88)	6.4845(8)	3.2440(6)	2.361(4)

behavior although it has a remarkable $S_T = 11/2$ ground state induced by an intramolecular Ni...Gd ferromagnetic interaction. On the other hand, replacing Gd with Dy restores the SMM behavior in Ni₂Dy complex as a result of the high-spin ground state of the complex and the mag-

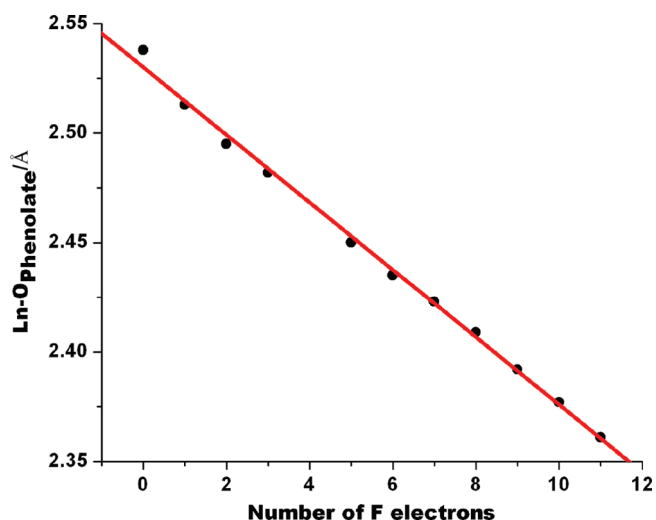


FIGURE 10. Ln–O_{phenolate} distance following the lanthanide contraction. Reproduced with permission from ref 44. Copyright 2009 American Chemical Society.

netic anisotropy brought by the Dy(III) metal ion. The magnetic behavior of the remaining Ni₂Ln compounds show that these are paramagnetic systems.⁴⁴

We have also been able to prepare the first examples of trinuclear Mn₂Ln [Ln = Eu (**89**), Gd (**90**), and Dy (**91**)] complexes utilizing the above strategy. These complexes are paramagnetic and show weak ferromagnetic interactions for the Mn^{II}/Gd^{III} and the Mn^{II}/Dy^{III} complexes at low temperature.⁴⁵

V. Outlook

Although it has been 85 years since Alfred Werner was given the Nobel prize for putting coordination compounds on the map of chemistry, the design and assembly of new ligands for interaction with transition metal ions continue to be a central theme in this area and will remain so for many more years. Ligand design influences the nature of metal assembly, their structure, and properties and hence impacts not just coordination chemistry but many areas influenced by it including organometallic chemistry, catalysis, bioinorganic chemistry, and materials. In this context, main group element supported ligand systems have considerable potential. Already boron-supported ligands, particularly the pyrazolyl borates, have proven themselves as extremely versatile. Other families such as phosphorus-supported ligand systems as detailed in this Account have been emerging only in recent years but have an exciting future. The challenges to be addressed in this area are the issues of discovering appropriate synthetic methods and controlling the number, nature, and stereochemistry of the coordination platforms supported by the main group element. Another issue is the stability of the ligands, which is related in part to the nature of the bond that connects the coordinating motifs with the main group element, although as we have shown in this Account, the sensitivity of the P–N bonds to hydrolysis under some situations can be utilized gainfully.

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Balasubramanian Murugesapandian (b. February 15, 1980, Virudhunagar, India) has obtained his M.Sc. in Chemistry from

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FOOTNOTES

[†]Dedicated to Prof. C. N. R. Rao on the occasion of his 75th birthday.

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