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Bimetallic Bis-anion Cascade Complexes of Magnesium in Nonaqueous Solution

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ABSTRACT: Bimetallic magnesium(II) complexes are gaining significant interest in catalysis, yet their fundamental formation and behavior in organic media remain surprisingly unexplored relative to other divalent cations. To understand key principles of their formation, we investigate symmetric ditopic ligands bearing a phenolic backbone and characterize their ability to form dinuclear magnesium(II) cascade complexes with two bridging anions. Highfidelity production of bimetallic magnesium complexes relative to the monometallic complexes is indicative of positive cooperativity. Binding and recognition of analytes or substrates is a key characteristic of metal cascade complexes and relies on anion exchange, but this is also rarely studied with bimetallic magnesium complexes. Investigations with acetate, phosphate, and pyrophosphate reveal exchange of bridging nitrates using the bisdipicolylamine complex. Rare seven-coordinate magnesium centers are found for the ester



complex. The findings in this study provide formative steps to establish design principles for future generations of bimetallic magnesium(II) complexes.

INTRODUCTION

Magnesium and its complexes are essential for life and are of longstanding importance in chemistry.^{1,2} Their roles can be seen in photosynthesis, the respiratory chain, and ATP consuming reactions¹⁻⁵ as well as the famous Grignard reaction, ⁶⁻¹⁰ which utilizes the reactivity of organyl-magnesium halides. Magnesium is now being considered as a low cost and low toxicity replacement for transition metals in catalysts for more environmentally friendly and "green" chemical processes.^{11,12} Emerging examples include ring-opening polymerizations,^{13–22} cycloadditions,^{23–27} redox-reactions,²⁸ addition or radical addition reactions,^{29–33} and hydroboration reactions³⁴⁻³⁸ as well as C-H and C-F activation.^{39,40} Fundamental knowledge of magnesium-ligand coordination chemistry and the supramolecular chemistry associated with the binding of substrates and of substrate analogs is a key aspect for the knowledge-driven design of new ligands. The catalytic species are generally assumed to be mononuclear magnesium complexes; however, dimers^{15,16,18-20,41-44} or multimers^{29,45-51} are often suggested. While these applications would benefit from comprehensive studies of magnesium complexation, such investigations are rare.⁵² Here we address this shortcoming with an investigation into some of the first cascade complexes of magnesium.

While there are over 150 examples of magnesium-catalyzed reactions, just 10% of these studies involve bimetallic magnesium complexes. Of these few, they have shown promise as catalysts in ring opening⁵³ and addition reactions^{33,54–56} as well as in polymerizations.^{57–64} The close proximity of the magnesium centers in these dinuclear complexes implies coordination of the substrate in a bridging fash-

ion^{53,55–57,59,61,62} as well as cooperative binding of two substrates at the same time.^{53–56,59,60} Fundamental binding studies describing how magnesium ions bind to ditopic ligands to produce complexes that are similar to these catalytic systems is even more rare. As a result, insights into their solution-phase behavior is severely lacking. Key qualities include their speciation and the existence of species of intermediate nuclearity in solution, the degree of cooperative binding of the two magnesium ions, and the behavior of the bimetallic magnesium complex upon substrate binding. NMR spectroscopy and detailed binding studies are often needed to address these features.

Examples of the coordination chemistry of magnesium are limited. Highly charged ligands, like ethylene diamine tetraacetic acid and its analogues, $^{65-68}$ are frequently used as magnesium chelators. However, these ligands are almost exclusively studied in aqueous media on account of their solubility and, therefore, are not helpful as models for processes like catalysis that are performed in organic solvents. Metal-cascade receptors, which are more structurally similar to bimetallic catalysts and which also serve as receptor-based sensors for anionic analytes like pyrophosphate or ATP, $^{69-75}$ are generally used in water and are also not ideal model

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candidates. Cascade complexes consist of metal centers that define ideal binding sites for counteranions. Negatively charged analytes can replace these counteranions resulting in spectral changes which makes them ideal for anion recognition. Transition metals like zinc(II),^{69–74,76,77} copper(II),^{77,78} and cobalt(III)⁷⁹ are frequently chosen to combine with bis-dipicolylamine-based ligands for these sensors instead of magnesium on account of the poor complex stability of magnesium complexes in water.^{76,80}

Mononuclear magnesium complexes of dipicolylamine have been studied previously as fluorescent probes for magnesium ions in acetonitrile.⁸⁰ Similar complexes and their dimers have been applied as catalysts in living lactide polymerizations in dichloromethane.²⁰ A magnesium complex of a bis-dipicolyamine-bearing ligand was briefly mentioned in a patent,⁸¹ but neither NMR nor solid state data was provided.

For all these reasons, studies of bimetallic magnesium complexes and their formation in organic media are of fundamental interest and are needed to help inform the development and design of next-generation catalysts and sensors. Investigations of the exchange of coordinating anions may also serve as surrogates for substrates and analytes to help close the gap in the fundamental understanding of these valuable complexes.

Herein we investigate the binding behavior of bimetallic magnesium complexes composed of ligands (Figure 1) bearing



Figure 1. Binding behavior of the various ligands toward bimetallic magnesium cascade complexes.

lone-pair donor atoms (N, O, S) and study the influence and exchange of bridging anions. The binding pockets share a central phenolic linker to enhance the binding strength of the magnesium ions. It is not known if coordination of two magnesium cations would show positive or negative cooperativity. It is also unknown if the metal centers bound by this ligand scaffold will be bridged by the counteranions of the magnesium salt used for the complexation or, in the case of bridging anions, if these anions can be exchanged or if metal extrusion occurs instead. We find that the binding pockets with pyridines and the esters enable competent binding with positive cooperativity favoring formation of the dinuclear magnesium complexes, while furan and thiophene lack good binding strengths. The pyridine-bearing complex forms a cleft between the magnesium centers occupied by two bridging nitrates. Use of the ester-derived ligands closes the cleft to generate nonbridging nitrate anions and results in a rare sevencoordinate pentagonal-bipyramidal coordination around each magnesium ion. Investigations of the exchange of bridging nitrates in the dinuclear magnesium complex of the pyridinebearing ligand were conducted with acetate, dihydrogen

phosphate, and hydrogen pyrophosphate. Our findings show that a variety of dinuclear magnesium(II) complexes are readily accessible and that bridging anions can be readily exchanged. These bimetallic bis-anion cascade complexes help take the first steps toward understanding the coordination chemistry of bimetallic magnesium complexes.

EXPERIMENTAL SECTION

Ligand Preparation. All ligands were prepared using a four-step pathway (Scheme 1). It is possible to reduce the number of steps

Scheme 1. Synthetic Route for the Preparation of Symmetric Ditopic Ligands a



^{*a*}DBU is used as base in the final step for ligands substituted with pyridine, triazole, furan, and thiophene. The IDA (iminodiacetic acid) ester bearing ligands are obtained using triethylamine as base.

either by benzylic bromination of 4-bromo-2,6-xylenol bearing a protected hydroxyl function^{82,83} or by a Mannich reaction starting from the commercially available 4-bromophenol **1** and the corresponding amines.^{82,84} However, the multistep route⁸² we followed involves three well-reported reactions^{85–87} and offers high ligand modularity by using simple nucleophilic substitution in the final step, which can also be easily monitored by ¹H NMR spectroscopy.

Starting with 4-bromophenol 1, a Duff reaction with hexamethylenetetramine in trifluoroacetic acid results in dialdehyde 2.^{85,86} After recrystallization, reduction with lithium aluminium hydride affords trialcohol 3.⁸⁵ Conversion of the benzylic alcohols into bromide leaving groups generates ligand precursor 4.⁸⁷ The three steps leading to 4 can be performed on multigram scales without resorting to timeconsuming purification methods. The final substitution reaction affords the target ligands in moderate to good yields. Bisdipicolylamine ligand L^{DPA}-H and methyl ester ligand L^{Me}-H are known compounds.^{84,88} The triazole-bearing amine is synthesized using click chemistry with dipropargylamine and phenylazide in good yields. The ligands bearing the various ester functionalities are obtained in good to very good yields from iminodiacetic acid (IDA) after esterification. pubs.acs.org/IC

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Figure 2. (a) The binding of bis-dipicolylamine ligand L^{DPA} -H upon addition of magnesium salt produces a putative mononuclear complex and the dinuclear species seen in the solid state. (b) The crystal structure of the bimetallic complex $[L^{DPA}Mg_2(\mu_2-NO_3)_2](NO_3)$ is shown with spacefill, (c) capped sticks, and (d) a side view with capped sticks and omitted nitrate counteranion. A single methanol molecule located in the unit cell is omitted for clarity in all three cases. (e) Solution binding (¹H NMR, 600 MHz) is observed in acetonitrile- d_3 upon addition of Mg(NO₃)₂(H₂O)₆ to L^{DPA} -H (5 mM, dilution corrected) at room temperature. Plotted curves for the changes are shown in the Supporting Information Figures S2 and S3.

Crystal Structures and Binding Behavior. Single crystals were grown from a methanol solution (L^{DPA} -H) or an acetonitrile solution with a 1:2 mixture of bis-dipicolylamine ligand L^{DPA} -H as well as ethyl iminodiacetate ligand L^{Et} -H and magnesium(II) nitrate hexahydrate by vapor diffusion of diethyl ether. The binding behavior in solution was observed using ¹H NMR spectroscopy following successive addition of magnesium(II) nitrate hexahydrate to the ligands. The ¹H NMR studies were carried out using 5 mM solutions of acetonitrile- d_3 at room temperature, and each aliquot addition is dilution corrected.

RESULTS AND DISCUSSION

Binding Behavior of Ligands Bearing Heterocyclic Rings. Based on prior studies of either cobalt⁷⁹ or zinc⁶⁹ with similar ligands, it is expected that two magnesium cations will bind into each of the binding pockets of the bis-dipicolylamine ligand L^{DPA} -H (Scheme 1). The nitrate counteranions are expected to bridge the magnesium centers as is seen with zinc cascade complexes of analytes like pyrophosphate.⁶⁹ The complex formed upon addition of magnesium(II) nitrate hexahydrate to the ligand, $[L^{DPA}Mg_2(\mu_2-NO_3)_2]^+$, fulfilled these expectations. This complex possesses a single positive charge (Figure 2a), which is ideal for observing the intact

cascade complex in the gas phase using electrospray ionization mass spectrometry (ESI-MS).

The crystal structure of $[L^{DPA}Mg_2(\mu_2-NO_3)_2](NO_3)$ shows two magnesium cations located in each binding pocket (Figure 2b-d). Each magnesium is coordinated by the three nitrogen atoms of the dipicolylamine units, and they share the deprotonated phenolic oxygen in the ligand backbone. The Mg...N average bond lengths of 2.19 Å are longer than the Mg...O bonds of 2.05 Å, which is consistent with the different valence state of the donor atoms. The torsion of the dipicolylamine units relative to the backbone creates a cleft between the magnesium centers that enables them to be bridged by the two nitrate anions. An additional nitrate serves as an outer-sphere counteranion.

Magnesium binding in acetonitrile- d_3 is consistent with the solid-state structure (Figure 2e). Two species are observed during titration with increasing amounts of magnesium nitrate hexahydrate. The first species generates downfield shifts in the ¹H NMR signals (pink, gray, cyan, and red). This shifting set of peaks is assigned to the formation of an intermediate 1:1 complex $[L^{DPA}Mg]^+$ in fast exchange with the free ligand (Figure S2). The intensity of this signature decreases with

addition of magnesium and is directly replaced by a slow exchanging species (green). This signature emerges upon addition of the initial 0.3 equiv aliquot of magnesium and grows continuously until saturation at 2 equiv. Splitting of the pyridyl signals into two sets is consistent with the two different pyridyl environments around each magnesium center as seen in the crystal structure. Consistent with lowered symmetry and slow exchange on the NMR time scale, the aliphatic signals split into four doublets for proton H_c and two doublets for proton H_b. Formation of the dinuclear complex is highly favored relative to the mononuclear complex. The positive cooperativity is seen in the direct formation of the dinuclear species from the beginning of the titration and the saturation at 2 equiv (Figures S1 and S3). The noncooperative situation would have shown formation of the dinuclear species only after production of the mononuclear, but that behavior was not observed.

The ESI-MS verifies the presence of both mononuclear and dinuclear complexes. Low resolution ESI-MS with substoichiometric amounts of magnesium (0.5 and 1 equiv) show signals of the mononuclear and dinuclear species together with the unbound ligand as either protonated species or sodium salts. The intensity of the signal for the dinuclear complex grows with increasing amounts of the magnesium salt (Figure S35). High resolution ESI-MS (Figure S38) matches the values and isotope pattern of the dinuclear magnesium complex $[L^{DPA}Mg_2(\mu_2-NO_3)_2]^+$ with m/z peaks of 765.1129 Da (⁷⁹Br isotope) and 767.1097 Da (⁸¹Br isotope). No evidence of a dimeric species involving two ligands was found by mass spectrometry. The nearly identical diffusion coefficients of the free ligand L^{DPA} -H ($D = 1.15 \times 10^{-9} \text{ m}^2/\text{s}$) and the final species $(D = 1.07 \times 10^{-9} \text{ m}^2/\text{s})$ are consistent with a nondimeric ligand structure.

The bimetallic complex $[L^{DPA}Mg_2(\mu_2 \text{-}NO_3)_2]^+$ is stable and maintained in solution for at least 2 weeks without decomposition as measured using NMR spectroscopy (Figure S4). It is also possible to prepare a solid form of the complex by removal of acetonitrile. The resulting green solid can then be redissolved in acetonitrile as well as in dichloromethane, which cannot be used directly to prepare the complex on account of solubility limitations (Figure S5).

The triazole ligand L^{triazole}-H shows a similar albeit weaker magnesium binding behavior (Figure S6). Splitting of the ¹H NMR signals for the dinuclear complex [L^{triazole}Mg₂(NO₃)₂]⁺ is found as soon as 0.3 equiv of magnesium(II) nitrate hexahydrate is added to the ligand. Those signals display a slow-exchange signature and grow in intensity during the titration (Figure S8). The mononuclear complex [L^{triazole}Mg]⁺ displays characteristic fast-exchange peaks that shift downfield until the addition of 1 equiv of the magnesium salt (Figure S7). A 1:2 ratio between the dinuclear and mononuclear complexes is present at 5 equiv of added magnesium nitrate indicative of the lower overall complex stability with triazoles.^{89–92} Mass spectrometry signals (Figure S39) are seen for the dinuclear magnesium complex [L^{triazole}Mg₂(NO₃)₂]⁺ at 1029.1990 Da (⁷⁹Br isotope) and 1031.1973 Da (⁸¹Br isotope). The furan ligand L^{furan}-H shows weak binding of

The furan ligand L^{furan}-H shows weak binding of magnesium. The slow-exchanging signature in the ¹H NMR typical of the dinuclear magnesium complex is not observed (Figure S9). Consequently, magnesium binding is assumed to proceed in a 1:1 fashion or to speciate as a mixture. This assignment is consistent with the small shifts of the observed NMR signals. Its sulfur analog, the thiophene bearing ligand

 $L^{\text{thiophene}}$ -H, results in nearly no magnesium binding (Figure S11). This observation is in line with the hard and soft acids and bases concept. Magnesium, as a hard acid, disfavors sulfur.

Binding Behavior of Ligands Bearing IDA (Iminodiacetic Acid) Esters. In general, we observe weaker binding of magnesium with the IDA ester ligands than with the bisdipicolylamine ligand L^{DPA} -H. The methyl ester L^{Me} -H shows only a fast exchange ¹H NMR signature upon magnesium addition (Figure 3a). This observation leads to the assumption





that the major species in solution is the mononuclear magnesium complex $[L^{Me}Mg]^+$ and that the ligand is not well suited for significant magnesium binding. Crystallization from either methanol or acetonitrile only results in magnesium(II) nitrate.

A significant change in the binding behavior is observed when using the ethyl and isopropyl esters, $L^{Et/iPr}$ -H. This change in affinity is assumed to be related to the enhanced inductive effect resulting in a higher electron density at the carbonyl oxygen of the esters. Upon addition of magnesium, an extra signal appears in the aromatic region (green box, Figures 3b and 3c). The intensity of this peak increases with the



Figure 4. Crystal structure of the dinuclear complex $[L^{Et}Mg_2(NO_3)_2(H_2O)_2](NO_3)$ with omitted solvent molecules. (a) Structure of the crystallized complex. (b) Side view with capped sticks and omitted outer-sphere nitrate counteranion. (c) Top view with spacefill. (d) Seven-coordinate pentagonal-bipyramidal magnesium center. (e) View along the plane of the phenol backbone showing the difference between the orientations of the ester chain of $[L^{Et}Mg_2(NO_3)_2(H_2O)_2]^+$ (left) and the pyridine units of $[L^{DPA}Mg_2(\mu_2-NO_3)_2]^+$ (right).

amount of added magnesium(II) salt (Figures S17 and S20) alongside a fast-exchange process (Figures S16 and S19) that resembles the signature seen with the methyl ester L^{Me}-H. No new signals arise in the aliphatic region. Rather they appear to be too broad to be readily assigned. Aggregation is inconsistent with the broad aliphatic signals on account of nearly identical diffusion coefficients for the peaks at 7.32 ppm (green box, Figure 3c) and 7.38 (pink, Figure 3c). Fortuitously, the broad aliphatic signals emerge more visibly with the isopropyl ester complex and sharpen up at lower temperature with consistent peak intensities (Figure S21). This observation is the first indication of the dinuclear magnesium complex seen previously in the slow-exchanging signature with L^{DPA}-H. Mass spectrometry shows signals of the dinuclear magnesium complexes in all cases (Figures S40-S42) with m/z values of 689.0271 and 691.0251 Da for [L^{Me}Mg₂(NO₃)₂]⁺, 745.0894 and 747.0877 Da for $[L^{Et}Mg_2(NO_3)_2]^+$, and 801.1523 and 803.1506 Da for $[L^{iPr}Mg_2(NO_3)_2]^+$. The benzyl ester ligand L^{Bz} -H binds weaker than the ethyl or isopropyl ester $L^{Et/iPr}$ -H but stronger than the methyl ester L^{Me}-H. The same slowexchanging aromatic signal is found for the dinuclear complex $[L^{Bz}Mg_2(NO_3)_2]^+$ but with a lower overall intensity (Figures S22 and S24). Values of 993.1527 and 995.1513 Da are seen in the ESI-MS (Figure S43) for the dinuclear complex $[L^{Bz}Mg_2(NO_3)_2]^+$. A 5-fold excess of magnesium salt was used for the gas phase experiments with the ester ligands on account of their weaker binding behavior.

We obtained the crystal structure of the ethyl IDA ester ligand as a dinuclear magnesium complex $[L^{Et}Mg_2(NO_3)_2(H_2O)_2](NO_3)$. We now see that the coordinating nitrates are no longer bridging the metal centers. The structure also possesses magnesium centers that are in a rare seven-coordinate geometry with distorted pentagonal-bipyramidal coordination (Figure 4a, d). In contrast, the structure of $[L^{DPA}Mg_2(\mu_2-NO_3)_2](NO_3)$ displays two six-coordinate octahedral magnesium centers (Figure 2b-d). Only one sevencoordinate magnesium with six oxygen and one nitrogen atoms in the inner coordination sphere has been reported⁹³ in the Cambridge Structure Database, which is composed of an azacrown ether complex. Just a dozen similar structures⁹⁴⁻¹⁰² with seven-coordinate magnesium centers are known that involve oxygen and more than one nitrogen atom. The bond lengths are slightly longer than the ones of the dipicolylamine complex $[L^{DPA}Mg_{2}(\mu_{2}-NO_{3})_{2}](NO_{3})$ with 2.4 Å (N···Mg) and 2.16 Å (O...Mg). Torsion of the IDA ester units is observed for the complex (Figure 4b, c) as was also seen with bis-dipicolylamine $[L^{DPA}Mg_2(\mu_2-NO_3)_2](NO_3)$. However, the ester groups of each IDA ester unit behave very differently in comparison to the pyridine units of the bis-dipicolylamine structure. An interplay of electronic and steric effects is assumed to be the reason for the seven-coordinate magnesium centers. The ester possesses weaker electron donating properties than pyridine. In addition, the ester has a strong electron-withdrawing effect, that is expected to weaken the ligating power of the central tertiary nitrogen more so than pyridine groups would. The weaker binding strength of the aliphatic nitrogen atom is reflected in a 0.2 Å increase of the bond length to magnesium $((CH_2)_2 N \cdots Mg: 2.40 \text{ Å in } [L^{Et} Mg_2 (NO_3)_2 (H_2 O)_2]^+ \text{ vs } 2.20 \text{ Å}$ in $[L^{\overline{DPA}}Mg_2(\mu_2-NO_3)_2]^+$). The steric effect reveals itself in the distorted structure. Within the equatorial plane, the two ester oxygen atoms that are located trans to each other define a O-Mg–O angle of 143° , which is much less than the ideal 180° . Also, the ester chains of both of the IDA ester units are oriented in a linear fashion at an angle of 171° between the two planes spanned by the $CH_2C=O$ unit of the ester instead of the orthogonal (84°) arrangement seen with L^{DPA} (Figure 4e). This span and the 143° O-Mg-O angle in the equatorial plane provide greater room for the nitrate to coordinate through two of its oxygen atoms with a tight O-Mg-O bite angle of 58° instead of just one oxygen atom. Electronic demands and steric access are thus responsible for expanding the donor atom set to seven.

Exchange of the Bridging Nitrate Anions in $[L^{DPA}Mg_2(\mu_2-NO_3)_2]^+$. Exchange of bridging anions is a key

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Figure 5. (a) Anion exchange reaction of the bridging nitrate groups by acetate added as the tetrabutylammonium salt in acetonitrile- d_3 . (b) The crystal structure is shown with omitted solvent in spacefill. The nitrate counteranion is hidden behind the upper pyridine ring. (c) Top view with capped sticks and (d) side view with omitted nitrate counteranion. (e) ¹H NMR solution spectra (600 MHz, 5 mM, dilution corrected) following the exchange of bridging nitrate for bridging acetate observed in acetonitrile- d_3 solution at room temperature.

characteristic of metal-cascade complexes though this behavior has never been studied previously with bimetallic magnesium complexes using NMR spectroscopy. The capability of anion exchange of the bis-dipicolylamine complex $[L^{DPA}Mg_2(\mu_2-NO_3)_2]^+$ was investigated by evaluating the ability of different anions to bridge the magnesium cations. Anion exchange studies were undertaken by starting with the dinuclear nitratebridged magnesium complex $[L^{DPA}Mg_2(\mu_2-NO_3)_2]^+$. Tetrabutylammonium salts of acetate (Figure 5a), dihydrogen phosphate, and hydrogen pyrophosphate (Figures S25, S30, S31, and S33) were examined.

Crystals obtained after the addition of 2 equiv of acetate verify the exchange. Acetate is now occupying the role of bridging anions in the complex $[L^{DPA}Mg_2(\mu_2\text{-}OAc)_2](NO_3)$, which retains an outer-sphere nitrate as counteranion (Figure 5b–d). The same slightly distorted octahedral geometry around the magnesium centers is seen with the acetate bridged structure compared to the nitrate bridged one. Very similar average N…Mg distances of 2.23 Å and O…Mg distances of 2.02 Å are found. The same cleft is created between the magnesium centers, which is occupied by the bridging acetate anions.

The crystal structure is consistent with anion exchange occurring in solution (Figure 5e). Addition of the acetate salt leads to the evolution of a new slow-exchanging species (marked in pink), which is highly favored after addition of the 2 equiv of acetate. With higher equivalents of acetate, none of the initial nitrate bridged complex $[L^{DPA}Mg_2(\mu_2 \text{-NO}_3)_2](NO_3)$ (green signals) nor any intermediate species are present (Figure S25). These observations show the favored exchange

of bridging nitrate by acetate. Addition of a large excess of tetrabutylammonium acetate and nitrate to the acetate-bridged complex was investigated in order to see different binding modes or anion exchange back to nitrate. Excess acetate salt led to the emergence of a new set of signals, which shows that the binding mode can be changed. However, more than 20 equiv of additional acetate were necessary to observe the new species, and the original acetate-bridged complex $[\mathbf{L}^{\text{DPA}}\text{Mg}_2(\mu_2\text{-OAc})_2]^+$ remains the main species (Figure S26). Addition of the nitrate salt does not show any change even after the addition of 50 equiv. As a result, the acetate-bridged complex is very stable (Figure S27).

Addition of 2 equiv of tetrabutylammonium dihydrogen phosphate results in a similar trend. Shifted signals show the exchange of nitrate for phosphate and the formation of the putative phosphate-bridged species $[L^{DPA}Mg_2(H_xPO_4)_2]^{(-3+2x)}$ as a major product, but a significant amount of an intermediate species remains visible in the ¹H NMR spectra (Figure S30). Addition of excess phosphate leads, in contrast to the acetate salt, to the formation and precipitation of a colorless solid. ³¹P NMR matches the findings, and two complexes involving phosphate are observed (Figure S31). This solid is assumed to be magnesium phosphate based on the recovery of the signals for the unbound ligand L^{DPA}-H. Titrations with magnesium acetate tetrahydrate and magnesium hydrogen phosphate trihydrate are not possible in the same way as the titrations conducted with magnesium nitrate hexahydrate on account of poor solubility. The anion exchange experiments show that the acetate complex is stable in solution. For this reason it should be possible to form the acetate complex by direct addition of

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magnesium acetate. We investigated different methods to determine if the formation of a magnesium complex occurs. Magnesium acetate tetrahydrate and magnesium hydrogen phosphate trihydrate were added into NMR tubes as solids. A solution of the ligand in deuterated acetonitrile (5 mM) was added to the salt in different stoichiometries. NMR spectra show that complex formation with magnesium acetate is very slow. Sonication and heating for 3 h showed that the same complex observed by anion exchange can be formed with magnesium acetate tetrahydrate (Figure S28). A time-dependent study shows that complex formation takes around 3 days if no external stimulus is applied (Figure S29). The samples with magnesium hydrogen phosphate trihydrate, on the other hand, show no complex formation even after applying an external force (Figure S32). Addition of pyrophosphate (TBA₃·HP₂O₇) acts in an even more extreme way, which is likely a result of its higher negative charge. Precipitation of an insoluble salt is observed with signals for the free ligand L^{DPA}-H dominating the ¹H NMR spectra after addition of 2 equiv of the pyrophosphate salt (Figure S33).

CONCLUSION

Magnesium binding to a series of ditopic ligands bearing a shared phenolic oxygen favor dinuclear complexes, and they can accommodate bridging and exchangeable anions depending on ligand structure. Putative mononuclear complexes are less favored and display fast-exchange signatures on the NMR time scale. Crystal structures reveal two nitrate anions bridging the two magnesium centers and residing in a central cleft defined by the dipicolylamine units of ligand LDPA-H. No bridging occurs in the case of the ethyl ester ligand, which is attributed to a near linear arrangement of the ester groups on the periphery of the backbone that closes the cleft between the metal centers. Anion exchange of the bridging anions in the dinuclear magnesium complex of dipicolylamine ligand L^{DPA}-H shows the potential for in situ variation of the coordination sphere in this magnesium cascade complex. Acetate shows direct exchange, while phosphate and pyrophosphate lead to disassembly of the complex upon precipitation of all-inorganic salts. This fundamental study opens up ways for the in situ generation of dinuclear magnesium complexes with high modularity. The difference in the nitrate-bridged $[L^{DPA}Mg_2(\mu_2-NO_3)_2]^+$ and nonbridged complex $[L^{Et}Mg_2(NO_3)_2(H_2O)_2]^+$ is of interest for the ligandcontrolled variation in the magnesium coordination sphere as a result of the closure of the cleft between the metal centers. The close proximity between the coordinating nitrate anions and the ester residue in $[L^{Et}Mg_2(NO_3)_2(H_2O_2)]^+$ may serve as the basis of chiral esters to investigate asymmetric transformations. These types of insights result from the fundamental investigation of the coordination chemistry and cascade complexation phenomena of magnesium ions in nonaqueous solution.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03710.

Synthetic methods and characterization data, NMR solution data for magnesium binding, NMR solution data for anion exchange experiments, ESI mass spectrometry data, and associated crystallographic

information for crystal structures (CCDC 1972635-1972637) (PDF)

Accession Codes

CCDC 1972635-1972637 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif, or by emailing data request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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