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Synthesis and Structural Characterization of Some New Magnesium Formamidinates

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Abstract. [Mg(Form)₂(THF)] [Form = bis(2,6-dimethylphenyl)formamidinate (XylForm) (1), bis(2,6-diethylphenyl)formamidinate, (EtForm) (2), bis(2,6-diisopropylphenyl)formamidinate (DippForm) (3)] are conveniently synthesized by treating bis(2,6-dimethylphenyl)formamidine, bis(2,6-diethylphenyl)formamidine, or bis(2,6-diisopropylphenyl)formamidine, respectively, with half an equivalent of dibut-

Introduction

Organomagnesium compounds have enjoyed a rich success over the last 100 years or so, mainly due to the ubiquitous nature of Grignard reagents and their utility in organic synthesis.^[1] Organoamidomagnesium compounds have been less studied.^[2] Recently, there have been a number of structural studies,^[3] and the reactivity of these compounds have also been investigated.^[4] Magnesium amidinates (Figure 1) are a subclass of these organoamidomagnesium compounds and while a number of examples have been studied with R_2 =Me (acetamidinates),^[5a,5b] Ph (benzamidinates),^[3a,5a,6] or NR''₂ (guanidinates),^[4a,7] there have been relatively few formamidinates (R_2 = H) in the literature.^[8]



Figure 1. A general amidinate ligand (left) and the ligands used in this paper [right: R = Me (XylForm), Et (EtForm), *i*Pr (DippForm)].

Indeed, we have extensively studied the structural chemistry of the alkali metal formamidinates as precursors to lanthanoid and other main group formamidinate complexes and while we have shown that magnesium mono- and bis(formamidinates) can be prepared,^[8b,8c] we have not studied these as extensively as alkali metal,^[9] heavier alkaline earth,^[10] *p*-block^[11] or *f*block counterparts.^[12] The use of magnesium reagents instead ylmagnesium in THF. Compounds 1-3 are mononuclear species in the solid state with five coordinate central metal atoms. The ¹H NMR chemical shift of the formamidinate formyl proton exhibits a correlation with ligand sterics wherein increasing bulk leads to a shift to higher field.

of alkali metal reagents in metathesis reactions can sometimes be beneficial, especially if the alkali metal reagents are too strongly reducing. Synthetic approaches to magnesium amidinates and guanidinates have been by a wide range of routes and all are generally high yielding, for example (i) protolysis of an amidine with a Grignard reagent;^[8a] (ii) redistribution of a CpMg(amidinate) to $MgCp_2$ and $Mg(amidinate)_2$ (Cp = C_5H_5 ;^[13] (iii) treatment of [Bi(DippForm)Cl₂] [DippForm = bis(2,6-diisopropylphenyl)formamidinate] with Mg metal;^[8c] (iv) treatment of $[Mg(N(SiMe_3)_2)_2]$ with nitriles;^[6c] (v) treatment of an amidine with dibutylmagnesium;^[6d,8b] (vi) treatment of a lithium amidinate with iPrMgCl;[5b] and (vii) treatment of Mg R_2 with a carbodiimide.^[5a,5c] We have shown that a very high yielding approach to low steric demand bis(p-tolylformamidinate)magnesiums (Figure 1, left, $R_1 = p$ -tolyl, $R_2 =$ H; p-TolForm) is through treatment of the p-TolFormH with half an equivalent of dibutylmagnesium [route (v) above],^[8b] and this is the approach we have used to extend the family of magnesium formamidinates to those with much higher steric demands herein. The only magnesium complexes involving formamidinate ligands are the amido Grignard reagent, [Mg(µ-Cl)(DippForm)(thf)]2^[8c] and those with very limited steric hindrance, viz. [Mg₂Cl₂(PhForm)(THF)₃](PhForm=bis(phenyl)formamidinate),^[8a] $[Mg(p-TolForm)_2(solvent)_n]$ (solvent = THF, n = 2; solvent = dme, n = 1; solvent = tmeda, n = 1) and $[Mg(o-TolForm)_2(solvent)_n]$ [o-TolForm = bis(o-tolyl)formamidinate; solvent = THF, n = 2].^[8b]

As part of a systematic study of the organoamido chemistry of the formamidinates we now report three magnesium complexes involving bis(2,6-dialkylphenyl)formamidinate ligands: $[Mg(Form)_2(THF)]$ [Form = bis(2,6-dimethylphenyl)formamidinate (XylForm) (1); bis(2,6-diethylphenyl)formamidinate, (EtForm) (2); bis(2,6-diisopropylphenyl)formamidinate, (DippForm) (3)] where the alkyl groups on the 2,6-positions of the ligand *N*-aryl can potentially influence the coordination

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number and arrangement of the central metal atom as we have observed in lanthanoid chemistry^[12] and the closely related chemistries of the heavy alkaline earth formamidinates.^[10] The data presented confirms the expected decline in coordination number for magnesium upon transitioning to *N*-2,6-dialkylphenyl substituents vis-à-vis smaller *N*-phenyl, *N*-*p*-tolyl, or *N*-o-tolyl formamidinates, and a shift to higher field in NC(*H*)N ¹H NMR resonance with increasing *N*-2,6-dialkylphenyl bulk. A similar spectroscopic trend is observed when transitioning from higher to lower coordination numbers or upon moving from the heavier alkaline earth formamidinates, e.g. Sr and Ba, to their calcium or magnesium counterparts.

Results and Discussion

Syntheses and Spectroscopic Characterization

[Mg(Form)₂(THF)] [Form = bis(2,6-dimethylphenyl)formamidinate (XylForm) (1); bis(2,6-diethylphenyl)formamidinate, (EtForm) (2); bis(2,6-diisopropylphenyl)formamidinate, (DippForm) (3)] were conveniently synthesized by treating two equivalents of bis(2,6-dimethylphenyl)formamidine, bis(2,6-diethylphenyl)formamidine, or bis(2,6-diisopropylphenyl)formamidine, respectively, with dibutylmagnesium in THF (Scheme 1). The isolated yields of each reaction were moderately good, except 3, where the enhanced solubility of the compound made its complete isolation in high purity more difficult. The thermal stability of each compound is excellent with no discernible decomposition up to 200 °C, with compound **2** decomposing soon thereafter (213 °C), compound **1** decomposing at 286 °C, and compound **3** decomposing at 314 °C. All compounds retain a metal-bound THF upon standing and their C,H,N analyses reflect the composition determined by X-ray diffraction methods vide infra.



Scheme 1. Synthesis of compounds 1-3 [R = Me(1), Et(2), *iso*propyl (3)].

Resonance signal integrals in the ¹H NMR spectra of **1–3** also indicate the robust coordination of THF at magnesium. The infrared spectra of all three complexes exhibit no absorptions for an N–H stretch indicating complete deprotonation of the respective formamidines and exhibit moderate to strong C–N stretches for the chelated formamidinate ligands between 1661 and 1538 cm⁻¹ and C–O stretches for coordinated THF at approximately 1025 cm⁻¹ (asymmetric) and 805 cm⁻¹ (symmetric). By comparing the ¹H NMR chemical shift of the NC(*H*)N function for compounds **1–3** and those of related alkaline earth compounds previously prepared by us,^[8b,8c,10] there is a clear trend between the frequency of the NC(*H*)N

Table 1. ¹H NMR spectroscopic data in C_6D_6 for the formamidinate NC(*H*)N resonances of the compounds presented in this work and some data for selected alkaline earth formamidinate compounds reported by us. All structures are mononuclear and all formamidinate ligands are *N*,*N'* chelating.

Metal	Ligand	Donor	¹ H NC(H)N /ppm	IR /cm ⁻¹	¹³ C NCN /ppm	Reference
Mg	pTolForm	THF ₂	8.61	1670s	161.1	[8b]
Mg	oTolForm	THF ₂	8.58	1674 s	163.9	[8b]
Mg	XylForm	THF_1	8.08	1651 m 1590 m	165.6	this work
Mg	DiepForm	THF_1	7.86	1538 m 1645 m	162.4	this work
6	Ĩ	1		1600 m 1567 m		
Mg	DippForm	THF_1	7.82	1661 m 1589 m	162.0	this work
Ca	XylForm	THF ₂	7.75	1539s 1651 m 1595 m	174.7	[10b]
Ca	oTolForm	THF ₂	8.39	1531 m 1668 m 1588 m	162.1	[10b]
Ca	DippForm	THF_1	8.16	1664 m 1592 m	169.4	[10a]
Ba	DippForm	THF ₂	8.17	1520 m 1666 m 1593 m	166.9	[10a]
Sr	DippForm	THF ₂	8.12	1528 s 1666m 1593 w 1530 s	168.5	[10a]

resonance (Table 1) and the steric congestion about the central metal atom. The NC(*H*)N resonance is shifted to higher field as the steric bulk of the ligand (leading to congestion about the metal centre along with coordinated THF) increases. For example, in moving from compounds **1** to **2** to **3** we see an NC(*H*)N⁻¹H NMR resonance shift from 8.08 to 7.86 to 7.82 ppm, respectively, as the steric bulk of the ligand is increased. When comparing these chemical shifts with those of the magnesium complexes with much less sterically demanding ligands, e.g. the aforementioned *o*-TolForm and *p*-TolForm [MgL₂(THF)₂] complexes (cf. increased coordination number), there is a marked downfield shift of the same resonance to 8.58 and 8.61 ppm, respectively.^[8b]

This trend is also evident for calcium, strontium, and barium complexes involving these ligands where, for example, arguably the most sterically crowded calcium complex; [Ca(Xyl-Form)₂(THF)₂] has a ¹H NMR NC(H)N resonance at δ = 7.75 ppm vs. 8.39 ppm for the related bis-formamidinate bis-THF o-TolForm complex.^[10] The former represents the lowest formyl proton ¹H NMR chemical shift reported by us amongst all bis(formamidinate)alkaline earth compounds.^[8b,8c,10] It is feasible that the observed shift to higher field results from steric crowding, which leads to a decline in formamidinate to metal donation and therefore increased magnetic shielding of the formyl proton. Thus, a decline in formamidinate bulk and/ or a reduction in coordination number, as per the transition from **3** to **1** or from $[Mg(o-TolForm)_2(THF)_2]$ to **1** (Table 1) effects a downfield shift in the ¹H NMR NC(H)N resonance. A less striking but similar trend is observed for the ¹³C NMR NCN carbon resonances of 1-3, with signals at 165.6, 162.4, and 162.0 ppm, respectively.

X-ray Crystal Structures

Compounds 1–3 are isostructural, with compounds 1 and 2 crystallizing in the monoclinic space group $P2_1/n$ and compound 3 crystallizing in the triclinic space group $P\overline{1}$ (for selected bond lengths and angles see Table 2). In all compounds one whole mononuclear unit comprises the asymmetric unit of the structure in which the magnesium is five coordinate, being

Table 2. Selected bond lengths /Å and angles /° for compounds 1-3.

bound by two N,N'-chelating formamidinate ligands and one terminal THF ligand (see Figure 2 for 1 and Table 2).



Figure 2. X-ray crystal structure of $[Mg(XylForm)_2(THF)]$ (1) displayed close to the O–Mg vector and showing the triangular arrangement of O(1), C(17), and C(34) about Mg(1). Compounds 2 and 3 are isostructural with 1. Thermal ellipsoids are shown at the 50% level. The THF ligand is depicted as a wire-frame and hydrogen atoms are omitted for clarity. See Table 2 for selected bond lengths and angles for compounds 1–3.

The arrangement about the central magnesium atoms of 1-**3** is severely distorted for regular five coordinate polyhedra (e.g. trigonal bipyramidal or square pyramidal) due to the tight bite size of the N,N'-formamidinate chelate [N-Mg-N angles for the bidentate ligands range from 63.58(9) to $64.42(8)^{\circ}$]. If the carbon atom on the backbone of the formamidinate ligands is considered as a point donor, the magnesium atoms of 1-3may be considered as three coordinate with the sum of the C-Mg-C', C-Mg-O, and C'-Mg-O angles being 359.98° in each case giving almost perfect trigonal planar arrangements. The Mg-N bond lengths for 1-3 range from 2.0876(19) to 2.169(2) Å (av. = 2.125 Å), from 2.105(2) to 2.1462(19) Å (av. = 2.125 Å) and from 2.087(2) to 2.192(2) Å (av. = 2.143 Å), respectively. The averages of these suggest similar steric congestion for the ligands about 1 and 2, while the DippForm ligands of complex 3 exhibit greater disparities and are longer

[Mg(XylForm)					
₂ (THF)]		[Mg(EtForm) ₂ (THF)]		[Mg(DippForm) ₂ (THF)]	
Mg1-O1	2.0576(17)	Mg1–O1	2.040(2)	Mg1–O1	2.055(3)
Mg1–N1	2.0904(19)	Mg1–N1	2.1361(19)	Mg1–N1	2.191(2)
Mg1–N2	2.155(2)	Mg1–N2	2.112(2)	Mg1–N2	2.087(2)
Mg1–N3	2.169(2)	Mg1–N3	2.1462(19)	Mg1–N3	2.101(2)
Mg1–N4	2.0876(19)	Mg1–N4	2.105(2)	Mg1–N4	2.192(2)
Av. $Mg-N = 2.125$		Av. $Mg-N = 2.125$		Av. $Mg-N = 2.143$	
N1-C17	1.325(3)	N1-C21	1.314(3)	N1-C25	1.317(3)
N2-C17	1.317(3)	N2-C21	1.328(3)	N2-C25	1.318(3)
N3-C34	1.321(3)	N3-C42	1.314(3)	N3-C50	1.316(3)
N4-C34	1.322(3)	N4-C42	1.327(3)	N4-C50	1.314(4)
C17-Mg1-C34	150.27(8)	C21-Mg1-C42	150.38(9)	C25-Mg1-C50	150.76(10)
C17-Mg1-O1	105.06(8)	C21-Mg1-O1	105.68(9)	C25-Mg1-O1	104.76(10)
C34–Mg1–O1 $\Sigma = 359.98(24)$	104.65(8)	C42–Mg1–O1 $\Sigma = 359.98(27)$	103.92(9)	C50–Mg1–O1 $\Sigma = 359.98(30)$	104.46(10)



on average. Closer inspection of the Mg-N bond lengths in each compound indicates a degree of asymmetry, with one shorter and one longer Mg-N internuclear distance per formamidinate. While this may be suggestive of some Mg-N(amido) vs. Mg-N(amino) type binding, this is not reflected in the N-C bond lengths of the formamidinates, where the N-C bond lengths are essentially the same within three e.s.ds in each ligand in each compound. The average Mg-N bond lengths are shorter than those in the six coordinate but less sterically demanding complexes $[Mg(p-TolForm)_2(THF)_2]$ (av. = 2.157 Å) and $[Mg(o-TolForm)_2(THF)_2]$ (av. = 2.165 Å)^[8b] as might be expected. The Mg–O(THF) bond lengths in 1 to 3 [2.0576(17), 2.040(2) and 2.055(3) Å, respectively] are much shorter than those in the six coordinate analogues; 2.150 Å) $[Mg(p-TolForm)_2(THF)_2]$ (av. and [Mg(0- $TolForm_{2}(THF)_{2}$ (av. = 2.134(2) Å].^[8b] These data imply that, as expected, the XylForm, EtForm, and DippForm ligands are more sterically demanding than the p-TolForm and o-Tol-Form ligands leading to diminishing space in the metal coordination spheres of 1-3 for the coordination of a second THF ligand. Despite the substantial steric bulk of the DippForm ligand, it is not sufficient to invoke a solvent free composition. Indeed, as evidenced by the thermal stability of **3** vide supra, THF coordination is robust about this compound.

Conclusions

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We have shown that clean deprotonation of the formamidine ligands XylFormH, EtFormH, and DippFormH occurs upon treatment with half an equivalent of dibutylmagnesium in THF and that all three formamidinates generate mononuclear five coordinate species. In view of the observed correlation between the ¹H NMR chemical shift of the formyl NC(*H*)N proton and the steric bulk / coordination number of the observed [MgL₂(THF)_n] complexes (L = formamidinate, n = 1 or 2) it is likely that the five coordination of **1**–**3** is retained in C₆D₆ solution and that, likewise, the solid state compositions of the complexes listed in Table 2 are also maintained in *deutero*-benzene solution.

Experimental Section

General: The bis(aryl)formamidinate precursors HXylForm, HEt-Form, and HDippForm were synthesized according to the procedure of Roberts through the condensation of two equivalents of 2,6-dialkylaniline with triethylorthoformate in the absence of solvent with one drop of glacial acetic acid as catalyst.^[14]

Dibutylmagnesium (1.0 M in heptane) was purchased from Aldrich. Tetrahydrofuran (THF) was dried with sodium, freshly distilled from sodium benzophenone ketyl and freeze-thaw degassed prior to use. All manipulations were performed using conventional Schlenk or glovebox techniques in an atmosphere of purified nitrogen in flamedried glassware. Infrared spectra (4000–500 cm⁻¹) were recorded as Nujol mulls with a PerkinElmer 1600 Fourier transform infrared spectrometer. ¹H NMR spectra were recorded at 300.13 MHz and ¹³C NMR spectra were recorded at 75.46 MHz with a Bruker AC 300 spectrometer at 300K, with chemical shifts referenced to the residual ¹H or ¹³C resonances of the [D₆]benzene solvent. C, H and N elemental analyses were conducted by the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, Dunedin, New Zealand. Melting points were determined in sealed glass capillaries in a nitrogen atmosphere and are uncorrected.

General Preparation of $[Mg(Form)_2(THF)]$ [Form = Bis(2,6-dimethylphenyl)formamidinate (XylForm) (1), Bis(2,6-diethylphenyl)formamidinate (EtForm) (2), Bis(2,6-diisopropylphenyl)formamidinate (DippForm) (3): Dibutylmagnesium (0.50 cm³, 0.50 mmol) was added dropwise to a stirred colorless solution of bis(aryl)formamidine (1.00 mmol) in THF (25 mL) at -30 °C. Gradual warming of the solution to ambient temperature over a period of 1 h afforded a yellow solution that was filtered, concentrated in vacuo to incipient crystallization (< 5 cm), and left at room temperature to afford colorless prisms (1), hexagonal rods (2), or blocks (3) suitable for single-crystal X-ray diffraction structure determination. These were isolated by filtration and, in the specific cases of 1 and 2, further crops were obtained by placement of the supernatant at -10 °C overnight. Relevant details for each compound are listed below.

Compound 1 (*R* = Me): Yield 0.14 + 0.04 g (60%), m.p. 286 °C. $C_{38}H_{46}MgN_4O$: calcd. C 76.18, H 7.74, N 9.35%; found: C 75.42, H 7.15, N 8.99%. ¹H NMR: δ = 8.08 [s, 2 H, NC(*H*)N], 7.06 (d, 8 H, ³J_{HH} 7.4 Hz, *m*-ArH), 6.98 (t, 4 H, ³J_{HH} 7.4 Hz, *p*-ArH), 3.57 (m, 4 H, OCH₂), 2.29 (s, 24 H, CH₃), 1.34 (m, 4 H, CH₂). ¹³C NMR: δ = 165.6 (NCN), 147.8, 134.5, 126.3, 124.1 (s, ArCH), 67.6 (s, OCH₂), 25.5 (s, CH₂), 19.4 (*s*, CH₃). IR (Nujol): \tilde{v} = 1651 (m), 1590 (m), 1538 (m) (C–N str), 1019 (s), 803 (sh s) (C–O, asym and symm str) cm⁻¹.

Compound 2 (*R* = Et): Yield 0.15 + 0.08 g (65%), m.p. 213 °C (dec). C₄₆H₆₂MgN₄O: calcd. C 77.67, H 8.79, N 7.88%; found: C 76.98, H 8.67, N 7.50%. ¹H NMR: δ = 7.86 [br. s, 2 H, NC(*H*)N], 7.08 (m, 8 H, *m*-ArH), 6.99 (m, 4 H, *p*-ArH), 3.58 (m, 4 H, OCH₂), 2.83 (br. q, 16 H, CH₂CH₃), 1.50 (m, 4 H, CH₂), 1.18 (br. t, 24 H, CH₂CH₃). ¹³C NMR: δ = 162.4 (NCN), 149.5, 137.9 (s, ArC), 127.3, 122.8, 66.8 (s, OCH₂), 25.8 (s, CH₂), 18.6 (*s*, CH₃). **IR** (Nujol): \tilde{v} = 1645 cm⁻¹ (m), 1600 (m), 1567 (m) (C-N str), 1027 (s), 807 (m) (C-O, asym and symm str) cm⁻¹.

Compound 3 (*R* = *i***Pr**): Yield 0.11 g (27%), m.p. 314 °C (dec). C₅₄H₇₈MgN₄O: calcd. C 78.76, H 9.55, N 6.80%; found: C 78.98, H 9.34, N 6.82%. ¹H NMR: δ = 7.82 [s, 2 H, NC(*H*)N], 7.20–7.10 (m, 12 H, Ar*H*), 3.61 [sep, 8 H, ³J_{HH} 6.8 Hz, C*H*(CH₃)₂], 3.56 (obscured m, 4 H, OC*H*₂), 1.57 (m, 4 H, C*H*₂), 1.29 (d, 48 H, ³J_{HH} 6.8 Hz, C*H*₃). ¹³C NMR: δ = 162.0 (NCN), 149.7, 141.5, 124.7, 123.6 (ArC), 68.9 (OC*H*₂), 32.9 [CH(CH₃)₂], 25.7, 25.5 [CH(CH₃)₂ and CH₂]. **IR** (Nu-jol): \tilde{v} = 1661 cm⁻¹ (m), 1589 (m) 1539 (s) (C-N str), 1031 (s), 804 (m) (C-O, asym and symm str) cm⁻¹.

X-ray Diffraction Structure Determinations: Crystalline samples of compounds 1–3 were mounted in viscous hydrocarbon oil on glass fibres at -150 °C (123 K). Crystal data were obtained with an Enraf-Nonius Kappa CCD diffractometer. X-ray data were processed using the DENZO program.^[15] Structural solution and refinement was carried out using the SHELX suite of programs^[16] with the graphical interface X-Seed.^[17] All hydrogen atoms were placed in calculated positions using the riding model. Crystal data and refinement parameters are compiled below with selected bond lengths and angles provided in Table 2. In compounds 2 and 3 there are atoms with high thermal envelopes and these are those that are involved in disorder. Compound 3 has severely prolate carbon atoms on the methyls of the *iso*propyl groups as well as the THF molecule suffering from disorder. This disorder has been modelled for all atoms. Percentage occupancies

and numbering of methyls (of iPr) concerned, as well as a disorder of the THF over two sites are compiled in the cif. Compound **2** similarly has disorder problems (methyls of ethyl groups). This disorder was modelled (see cif).

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Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1420278 for compound **2**, CCDC-1420279 for compound **3**, and CCDC-1420280 for compound **1** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Crystal Data for Compound 1: $C_{38}H_{46}MgN_4O$, M = 599.10, colorless prism, $0.30 \times 0.20 \times 0.20$ mm³, monoclinic, space group $P_{2_1/n}$ (no. 14), a = 12.465(3), b = 15.016(3), c = 19.071(4) Å, $\beta = 108.53(3)^{\circ}$, V = 3384.5(12) Å³, Z = 4, $D_c = 1.176$ g·cm⁻³, F(000) = 1288, Nonius Kappa CCD, Mo- K_{α} radiation, $\lambda = 0.71073$ Å, T = 123(2) K, $2\theta_{max} = 56.6^{\circ}$, 23261 reflections collected, 8264 unique ($R_{int} = 0.0990$). Final GooF = 0.914, $R_1 = 0.0560$, $wR_2 = 0.1139$, R indices based on 3537 reflections with $I > 2\sigma(I)$ (refinement on F^2), 405 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.088$ mm⁻¹.

Crystal Data for Compound 2: $C_{46}H_{62}MgN_4O$, M = 711.31, colorless hexagonal rods, $0.40 \times 0.20 \times 0.20$ mm³, monoclinic, space group $P2_1/n$ (no. 14), a = 14.208(3), b = 15.970(3), c = 18.637(4) Å, $\beta = 100.86(3)^\circ$, V = 4153.4(14) Å³, Z = 4, $D_c = 1.138$ g·cm⁻³, F(000) = 1544, Nonius Kappa CCD, Mo- K_a radiation, $\lambda = 0.71073$ Å, T = 123(2) K, $2\theta_{max} = 56.6^\circ$, 38693 reflections collected, 9846 unique (R_{int} = 0.1370). Final GooF = 0.895, $R_1 = 0.0626$, $wR_2 = 0.1364$, R indices based on 3696 reflections with $I > 2\sigma(I)$ (refinement on F^2), 509 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.081$ mm⁻¹.

Crystal Data for Compound 3: $C_{54}H_{78}MgN_4O$, M = 823.51, block, $0.20 \times 0.10 \times 0.10 \text{ mm}^3$, triclinic, space group $P\overline{1}$ (no. 2), a = 11. 128(2), b = 13.661(3), c = 17.599(4) Å, a = 90.29(3), $\beta = 98.30(3)$, $\gamma = 69.36(3)^\circ$, V = 2474.5(8) Å³, Z = 2, $D_c = 1.105 \text{ grcm}^{-3}$, F(000) = 900, Nonius Kappa CCD, Mo- K_a radiation, $\lambda = 0.71073$ Å, T = 123(2) K, $2\theta_{\text{max}} = 56.6^\circ$, 26630 reflections collected, 11871 unique ($R_{\text{int}} = 0.0943$). Final *GooF* = 0.871, $R_1 = 0.0804$, $wR_2 = 0.1701$, R indices based on 4714 reflections with $I > 2\sigma(I)$ (refinement on F^2), 638 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.076 \text{ mm}^{-1}$.

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