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Synthesis and characterisation of aluminium and magnesium complexes supported by pendant oxalic amidinate ligands

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Received 13th February 2003, Accepted 13th May 2003
First published as an Advance Article on the web 23rd May 2003

Two pendant oxalic amidine compounds $[C_6H_5N{=}C\{NH(CH_2)_2OMe\}{-}C\{NH(CH_2)_2OMe\}{=}NC_6H_5]$ (**1**) (oxam(OMe)$_2$H$_2$) and $[C_6H_5N{=}C\{NH(CH_2)_2NMe_2\}{-}C\{NH(CH_2)_2NMe_2\}{=}NC_6H_5]$ (**2**) (oxam(NMe$_2$)$_2$H$_2$) are described. Reactions of **1** or **2** with two molar equivalents of $AlMe_3$ in toluene give the bimetallic complexes [(Me$_2$)Al(oxam(OMe)$_2$)Al(Me$_2$)] (**3**) and [(Me$_2$)Al(oxam(NMe$_2$)$_2$)Al(Me$_2$)] (**4**), respectively. Treatment of **1** or **2** with two molar equivalents of MeMgBr in THF affords the bimetallic complexes [(Br)(THF)Mg(oxam(OMe)$_2$)-Mg(THF)(Br)] (**5**) and [(Br)(THF)Mg(oxam(NMe$_2$)$_2$)Mg(THF)(Br)] (**6**) respectively. The crystal and molecular structures are reported for compounds **1**, **2**, **3**, **5** and **6**.

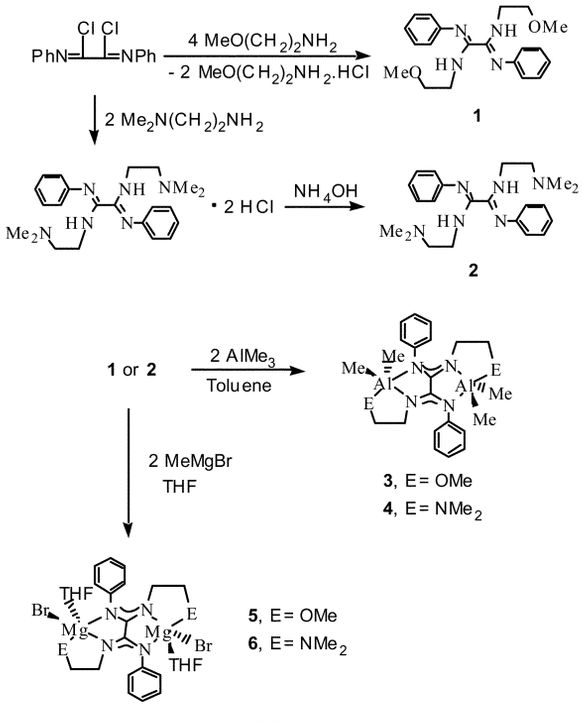
Introduction

Since the steric protection of the active site and influence over selectivity can be varied by the substituents on the N atoms, a number of research groups are investigating various main and transition metal complexes with bi- and multi-dentate nitrogen-based ligands in the coordination sphere.[1–4] The mono anionic nitrogen-based ligands, such as diketiminates, aminotroponiminates, and amidinates, which normally act as hard, four-electron-donors, are extensively being used as ancillary ligands in a large diversity of metal complexes and their structure and chemistry have been reviewed.[5–9] Among these three types of bidentate ligand, amidinates have been the most widely applied in coordination chemistry whereas the diketiminates and aminotroponiminates have received relatively less attention. Due to the steric and electronic properties of amidinato ligands they are easily programmable by variation of the substituents on either or both the N and C atoms; many amidinates with various substituents have been synthesized. Several types of amidinato ligands with pendant functionalities were found to act as three-coordinate, six-electron-donor ligands.[10–15] The amidinato ligands bridged *via* the C or N atoms of a CNN moiety have also been reported.[16–25] Recently oxalic amidinate complexes have attracted interest, mainly owing to the discovery of their application in catalytic reactions and their versatile bonding modes found in the various metal complexes.[34] In a similar fashion to amidine, the properties of these ligands can be programmed by the substituents on the nitrogen atoms. Neutral or anionic oxalic amidines show potential to work as diimine,[26–28] diimine-diamide,[28–33] or amidinate ligands.[34] Once the pendant functionality has been formed, the oxalic amidines have the potential to act as ligands that are up to three-coordinate, six-electron-donor on each side.[35–37]

In this paper, we report the preparation and structural properties of pendant oxalic amidines and their aluminium and magnesium complexes.

Results and discussion

The desired amidines can be prepared by the reactions of bis(imidoyl)chloride with the relevant amines, as shown in Scheme 1. Treatment of bis(imidoyl)chloride with 4 molar equivalents of 2-methoxyethylamine in toluene affords $[C_6H_5N{=}C\{NH(CH_2)_2OMe\}{-}C\{NH(CH_2)_2OMe\}{=}NC_6H_5]$ (**1**) (oxam(OMe)$_2$H$_2$) as a white solid. Crystals suitable for X-ray refinement were grown from toluene/hexane solution. The crystal structure of amidine **1** has been determined and the molecular structure is shown in Fig. 1. The interatomic distances and



Scheme 1

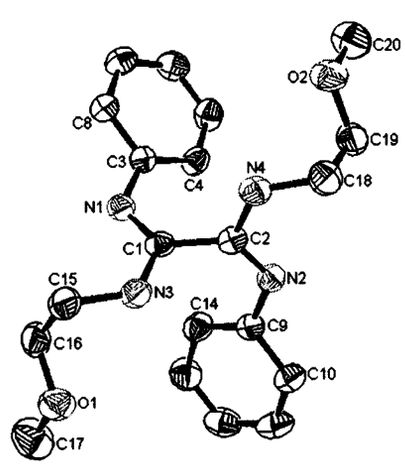


Fig. 1 Molecular structure of $[C_6H_5N{=}C\{NH(CH_2)_2OMe\}{-}C\{NH(CH_2)_2OMe\}{=}NC_6H_5]$ (**1**). Hydrogen atoms and toluene molecule omitted for clarity.

DOI: 10.1039/b301744c

Table 1 Selected bond lengths (Å) and angles (°) for **1**

N(1)–C(1)	1.288(3)	N(3)–C(1)	1.346(3)
N(2)–C(2)	1.281(3)	N(4)–C(2)	1.343(3)
N(1)–C(3)	1.418(3)	N(2)–C(9)	1.409(3)
N(3)–C(15)	1.443(4)	N(4)–C(18)	1.445(4)
C(1)–C(2)	1.499(4)		
C(1)–N(1)–C(3)	122.7(2)	C(2)–N(2)–C(9)	123.2(2)
N(1)–C(1)–N(3)	120.2(2)	N(2)–C(2)–N(4)	120.6(2)
C(1)–N(3)–C(15)	122.1(2)	C(2)–N(4)–C(18)	122.8(2)
N(1)–C(1)–C(2)	127.1(2)	C(2)–C(1)–N(3)	112.6(2)
C(1)–C(2)–N(2)	126.9(2)	C(1)–C(2)–N(4)	112.5(2)

angles are listed in Table 1. The structure displays a *trans*-(*E-syn*/*E-syn*) configuration.[38–39] The two CNN planes (N1–C1–N3 and N2–C2–N4 planes) intersect with a dihedral angle of 75.4°. No intra- or inter-molecular hydrogen bonds are found in this structure. However complex and broad signals, which are normally observed except in compound with intramolecular hydrogen bonds,[35] were found in the ^{1}H NMR. In order to study the tautomeric rotation of amidine, variable temperature NMR experiments of an analytically pure sample of compound **1** in toluene-d_8 were investigated.[40] Based on the integral intensity of the resonances from N*H*, two major species were found in a ratio of *ca*. 1.34 : 1 with tiny amounts of other species at room temperature. When a sample was heated to 363 ± 10 K, only one set of peaks corresponding to the symmetrical species was observed which, based on the crystallographic data, we assign as the *trans*-(*E-syn*/*E-syn*) isomer.[40] However, it is difficult to make the assignments upon cooling the sample below room temperature due to the complicated spectroscopic data for this oxalic amidine bearing two asymmetrical units in each side.

The possibility that hydrogen bonds between carboxylate-O and amidine-NH sites can force protonated amidine into an *E*/*E* configuration was explored by the reaction between amidine and benzoic acid in solution and was confirmed by the X-ray structure.[41–42] Therefore the reaction between **1** and benzoic acid in the mole ratio of 1 : 2 was investigated. The ^{1}H NMR spectrum of **1** becomes more simple and clear after the addition of benzoic acid in $CDCl_3$. No further impurity was found in the spectrum. The consequence of the carboxylate ligand forcing the amidine into an (*E*/*E*) configuration can work as a route to examine the purity of the amidine.

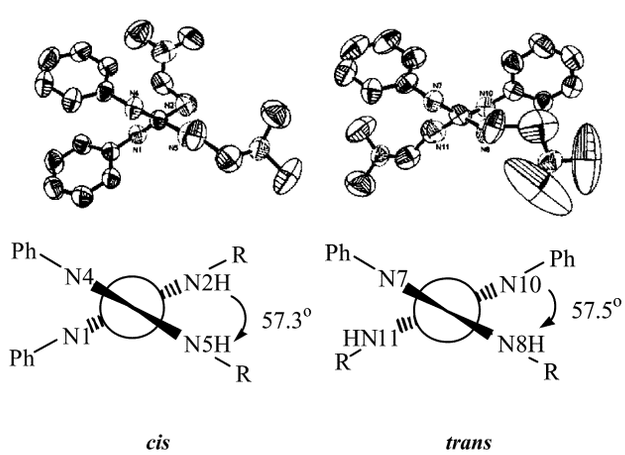
Compound **2** (oxam$(NMe_2)_2H_2$) was synthesized by treatment of bis(imidoyl)chloride with 2 molar equivalents of *N*,*N*-dimethylethyleneamine in toluene, followed by the addition of 25% aqueous ammonia to afford the free amidine **2** as an oily solid. The ^{1}H NMR spectrum shows more sharp signals than those observed for compound **1**, with a tiny amount of minor species, in chloroform-*d* solution. Similar to compound **1**, compound **2** also exhibits tautomeric rotation in solution. Peaks merge into one species upon heating to 323 ± 10 K, indicating a symmetrical species which, based on the discussion of compound **1**, we assign as the *trans*-(*E-syn*/*E-syn*) isomer. Crystals suitable for X-ray refinement were grown from a saturated hexane solution. The crystal structure of amidine **2** has been determined and the molecular structure is shown in Fig. 2. The interatomic distances and angles are listed in Table 2. The asymmetric unit of **2** contains two independent molecules in *E-syn*/*E-syn* configuration. Each molecule has a different conformation, one with the two Ph groups in *cis*-position and the other with the two Ph groups *trans*. The dihedral angles for each molecule are 57.3° (N1–C1–N2 and N4–C12–N5 planes) and 57.5° (N7–C31–N8 and N10–C42–N11 planes) that are smaller than that in compound **1** with a difference of 18°. This difference might result from the crowded environment caused by intermolecular H-bonding (2.286Å) between imine-N (N7) and amine (N2–H2A). The bridged C–C bonds for **1** (1.499(4) Å) and **2** (1.509(4) Å and 1.518(4) Å) are a bit shorter than that

Table 2 Selected bond lengths (Å) and angles (°) for **2**

N(1)–C(1)	1.294(4)	N(2)–C(1)	1.352(4)
N(4)–C(12)	1.283(4)	N(5)–C(12)	1.348(4)
N(1)–C(2)	1.399(4)	N(4)–C(13)	1.431(4)
N(2)–C(8)	1.450(4)	N(5)–C(19)	1.461(4)
C(1)–C(12)	1.509(4)	C(31)–C(42)	1.518(4)
N(7)–C(31)	1.283(4)	N(8)–C(31)	1.342(4)
N(10)–C(42)	1.281(4)	N(11)–C(42)	1.349(4)
N(7)–C(32)	1.415(5)	N(8)–C(38)	1.453(5)
N(10)–C(43)	1.414(4)	N(11)–C(49)	1.446(4)
C(1)–N(1)–C(2)	123.6(3)	C(1)–N(2)–C(8)	120.8(3)
N(1)–C(1)–N(2)	120.0(3)	N(1)–C(1)–C(12)	126.5(3)
N(2)–C(1)–C(12)	113.4(2)	C(12)–N(4)–C(13)	121.1(3)
C(12)–N(5)–C(19)	123.2(3)	N(4)–C(12)–N(5)	119.6(3)
N(4)–C(12)–C(1)	126.8(3)	N(5)–C(12)–C(1)	113.5(3)
C(31)–N(7)–C(32)	122.1(3)	C(31)–N(8)–C(38)	122.7(3)
N(7)–C(31)–N(8)	120.5(3)	N(7)–C(31)–C(42)	126.1(3)
N(8)–C(31)–C(42)	113.4(3)	C(42)–N(10)–C(43)	122.5(3)
C(42)–N(11)–C(49)	124.3(3)	N(10)–C(42)–N(11)	120.7(3)
N(10)–C(42)–C(31)	125.7(3)	N(11)–C(42)–C(31)	113.6(3)

Table 3 Selected bond lengths (Å) and angles (°) for **3**. The A atoms are generated by an inversion center

Al–N(1)	1.9374(16)	Al–N(2A)	2.0054(17)
Al–O	2.2243(17)	Al–C(5)	1.968(2)
Al–C(6)	1.975(2)	C(1)–C(1A)	1.523(3)
N(1)–C(1)	1.323(2)	N(2)–C(1)	1.317(2)
N(1)–C(2)	1.477(2)	N(2)–C(7)	1.435(2)
N(1)–Al–C(5)	120.35(9)	N(1)–Al–C(6)	116.39(9)
C(5)–Al–C(6)	121.47(11)	N(1)–Al–N(2A)	81.09(7)
N(2A)–Al–O	157.30(6)	N(1)–C(1)–N(2)	133.59(17)
N(2)–C(1)–C(1A)	112.5(2)	N(1)–C(1)–C(1A)	113.91(19)



cis ***trans***

Fig. 2 Two conformations found in the solid state of **2**.

(1.526(4) Å) in [2,4,6-Me_3–C_6H_2N=C{NH(CH_2)py}–]$_2$,[35] indicating a less bulky environment in **1** and **2**. Two significantly different sets of C–N bonds (1.281(3)–1.294(4) Å and 1.342(4)–1.352(4) Å) are found in each amidine fragment of both compounds, indicating the localized nature of the imine C=N and amine C–N bonds.

Both amidine ligands react readily with two molar equivalents of $AlMe_3$ in toluene to afford pure bimetallic complexes [(Me_2)Al(oxam$(OMe)_2$)Al(Me_2)] (**3**) and [(Me_2)Al(oxam$(NMe_2)_2$)Al(Me_2)] (**4**) with the concomitant elimination of methane. The ^{1}H and ^{13}C{^{1}H} NMR spectra of each compound are indicative of a highly symmetric species in solution. On the basis of these results, a penta-coordinated aluminium center was postulated for each of the two species.

Crystals of **3** suitable for X-ray refinement were grown from dichloromethane/hexane solution. The crystal structure has been determined and the molecular structure is shown in Fig. 3. The interatomic distances and angles are listed in Table 3. The structure confirmed a symmetric penta-coordinated aluminium

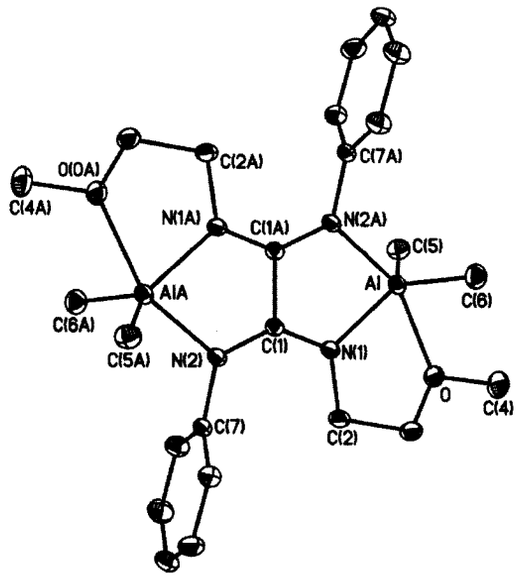


Fig. 3 Molecular structure of $[(Me_2)Al(oxam(OMe)_2)Al(Me_2)]$ (**3**). Hydrogen atoms on carbon omitted for clarity.

center with a planar amidine moiety. The ligand shows a *trans* configuration and prefers to form bis-five-membered metallacycles rather than bis-four-membered metallacycles upon coordination to the aluminium center. The two five-membered planes are co-planar with the two Al atoms and two amidine moieties. The central Al atoms adopt distorted trigonal bipyramidal geometry with distorted-axes O–Al–N2A (157.30(6)°). The N1(N1A), C5(C5A), and C6(C6A) atoms reside equatorially, forming angles subtended by aluminium of ≈120°. The bond lengths C1–N1 (1.323(2) Å) and C1–N2 (1.317(2) Å) are almost identical, indicating the delocalization of π-electrons around N1–C1–N2. The amidinate nitrogen–aluminium bonds (1.9374(16) and 2.0054(17) Å) are longer than that (1.906(3) Å) in $[(Me_2)Al(CH_3N)C(NCH_3)–(CH_3N)C(NCH_3)Al(Me_2)]$ whereas the bite angle (N1–Al–N2A = 81.09(7)°) is smaller than that (85.7(1)°) in $[(Me_2)Al(CH_3N)C(NCH_3)–(CH_3N)C(NCH_3)Al(Me_2)]$,[29] due to the steric effect of the substituents on the nitrogen atoms. The Al–Me bonds (1.968(2) and 1.975(2) Å) are within the ranges (1.94–2.03 Å) observed for relevant aluminium amidinate complexes.[11,29,40,43–45]

Treatment of **1** or **2** with two molar equivalents of MeMgBr in THF affords bimetallic complexes $[(Br)(THF)Mg(oxam(OMe)_2)Mg(THF)(Br)]$ (**5**) and $[(Br)(THF)Mg(oxam(NMe_2)_2)Mg(THF)(Br)]$ (**6**) with the concomitant elimination of methane. NMR spectroscopy indicates both compounds are highly symmetric species in solution. Likewise most magnesium amidinate complexes with a less crowded environment around the metal center display a tendency to coordinate solvents such as THF or PhCN,[46–49] two multiplets (for **5**: δ 1.57 and 3.69 ppm; for **6**: δ 1.61 and 3.75 ppm) corresponding to the coordinated THF are found in each compound. The elemental analysis data are also consistent with a complex containing coordinated THF.

Crystals of **5** were grown from THF/hexane solution. The crystal structure has been determined and the molecular structure is shown in Fig. 4. The interatomic distances and angles are listed in Table 4. The structure also confirmed a symmetric penta-coordinated magnesium center with a planar amidine moiety. Similar to the relevant aluminium compounds discussed above, deprotonated **1** is seen to act as a tridentate ligand on each side, binding to magnesium *via* two amidinate nitrogen atoms from different CNN units and one coordinated oxygen atom. The geometry at magnesium can be described as distorted trigonal bipyrimidal with O(1) and N(1A) occupying

Table 4 Selected bond lengths (Å) and angles (°) for **5**. The A atoms are generated by an inversion center

Mg–N(1A)	2.107(2)	Mg–N(2)	2.044(2)
Mg–O(1)	2.155(2)	Mg–O(2)	2.051(2)
Mg–Br	2.4823(9)	C(1)–C(1A)	1.536(4)
N(1)–C(1)	1.329(3)	N(2)–C(1)	1.316(3)
N(1)–C(2)	1.419(3)	N(2)–C(8)	1.463(3)
N(2)–Mg–O(2)	123.00(9)	N(2)–Mg–Br	131.99(7)
O(2)–Mg–Br	103.91(7)	N(1A)–Mg–N(2)	77.74(8)
N(1A)–Mg–O(1)	152.07(9)	N(1)–C(1)–N(2)	132.3(2)
N(2)–C(1)–C(1A)	112.8(2)	N(1)–C(1)–C(1A)	114.9(2)

Table 5 Selected bond lengths (Å) and angles (°) for **6**. The A atoms are generated by an inversion center

Mg–N(1A)	2.119(2)	Mg–N(2)	2.057(2)
Mg–N(3)	2.282(3)	Mg–O	2.050(2)
Mg–Br	2.5082(8)	C(1)–C(1A)	1.546(4)
N(1)–C(1)	1.330(3)	N(2)–C(1)	1.313(3)
N(1)–C(2)	1.423(3)	N(2)–C(8)	1.467(3)
N(2)–Mg–O	123.64(9)	N(2)–Mg–Br	131.26(7)
O–Mg–Br	104.78(7)	N(1A)–Mg–N(2)	77.28(8)
N(1A)–Mg–N(3)	153.95(9)	N(1)–C(1)–N(2)	132.6(2)
N(2)–C(1)–C(1A)	113.2(2)	N(1)–C(1)–C(1A)	114.2(2)

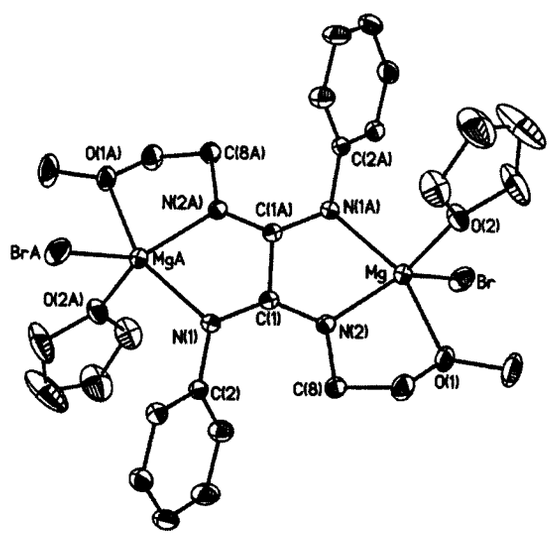


Fig. 4 Molecular structure of $[(Br)(THF)Mg(oxam(OMe)_2)Mg(THF)(Br)]$ (**5**). Hydrogen atoms on carbon omitted for clarity.

the axial positions (O(1)–Mg–N(1A) 152.07(9)°). The Br(BrA), O2(O2A) and N2(N2A) atoms reside equatorially, however with different angles (131.99(7)°, 123.00(9)°, 103.91(7)°) subtended by magnesium. The bond lengths of C1–N1 (1.329(3) Å) and C1–N2 (1.316(3) Å) are similar, consistent with the delocalization of π-electrons within the amidine moiety. The amidinate nitrogen–magnesium bonds (2.044(2) and 2.107(2) Å) are within the Mg–N single bond ranges (2.04–2.17 Å) found in magnesium amidinate complexes.[11,47–51] The coordinated THF oxygen–magnesium bond (Mg–O2 2.051(2) Å) is shorter than those (2.08–2.33 Å)[47–49] in magnesium amidinate complexes and the pendant-armed oxygen–magnesium bond (Mg–O1 2.155(2) Å) in the same molecule, but comparable to those Mg–O (coordinated-THF) bonds (2.042–2.092 Å) in Mg(diiminato)(X)(THF) (X = Me, O^{t}Bu, N^{i}Pr) complexes.[52–54]

Crystals of **6** were grown from dichloromethane/hexane solution and the crystal structure has been determined. The molecular structure is shown in Fig. 5 and the interatomic distances and angles are listed in Table 5. Basically, compound **6** is quite similar to compound **5** with different dative NMe_2 instead of OMe for **5**. Bond lengths and bond angles are similar to those discussed above. The pendant-armed nitrogen–magnesium bond (Mg–N3 2.282(3) Å) is longer than those found for the

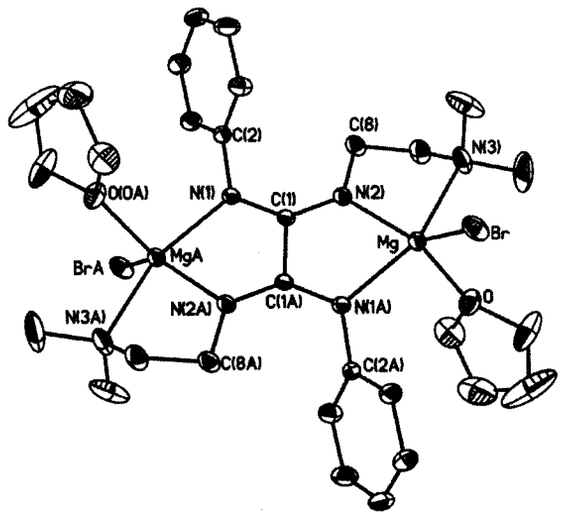


Fig. 5 Molecular structure of [(Br)(THF)Mg(oxam(NMe$_2$)$_2$)-Mg(THF)(Br)] (**6**). Hydrogen atoms on carbon omitted for clarity.

amidinate nitrogen–magnesium bonds (2.0406–2.168 Å), but comparable to the pyridine–magnesium bonds (2.260(4) and 2.264(4) Å) found in [2-Py–(CH$_2$)$_2$NC(*p*-MePh)NPh]$_2$Mg.[11]

In conclusion, novel oxalic-amidines with pendant functionalities can be easily accomplished. Similar to most other oxalic amidinato complexes these ligands prefer to form five-membered metallacycles upon coordination to aluminium or magnesium centers.

Experimental

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or drybox techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Deuterated solvents were dried over molecular sieves.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Varian Gemini-200 (200MHz), Varian VXR-300 (300MHz), Varian Mercury-400 (400MHz) or Varian Inova-600 (600 MHz) spectrometers in chloroform-*d* at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed by a Heraeus CHN-O-RAPID instrument.

Oxanilide (Acros), PCl_5 (RDH or Merck), benzoic acid (Showa), $AlMe_3$ (2 M in toluene, Acros) and MeMgBr (3 M in Et_2O, Aldrich) were used as supplied. 2-Methoxyethylamine and *N*,*N*-dimethylethylenediamine were dried over CaH_2 and distilled before use. Bis-phenylimidoylchloride was prepared by the literature method.[55]

Preparations

[C$_6$H$_5$N=C{NH(CH$_2$)$_2$OMe}–C{NH(CH$_2$)$_2$OMe}=NC$_6$H$_5$] (1) (oxam(OMe)$_2$H$_2$). A yellow solution of [C$_6$H$_5$N=C(Cl)–C(Cl)=NC$_6$H$_5$] (6.9 g, 25 mmol) in toluene (60 ml) was treated with 8.7 ml of 2-methoxyethylamine (7.5 g, 100 mmol) at 0 °C in a dropwise manner. The reaction mixture was stirred in an ice-bath for 1 h, and then allowed to warm to room temperature and react overnight. After 18 h of stirring, the resulting mixture was filtered and the filtrate was concentrated to around one forth volume. The concentrated filtrate was layered with *ca.* 20 ml hexane and stood at room temperature overnight to afford a white crystalline solid. Yield, 5.4 g, 60%. ^{1}H NMR (600 MHz, toluene-d_8, 363 K): δ 2.97 (s, CH_3, 6H), 3.02 (br, (CH_2)$_2$, 4H), 3.15 (br, (CH_2)$_2$, 4H), 6.84 (t, *p*-Ph, 2H,*J* = 7.8 Hz), 6.88 (br, *o*-Ph, 4H), 7.08 (t, *m*-Ph, 4H, *J* = 7.8 Hz). ^{13}C{^{1}H} NMR (150 MHz, toluene-d_8, 363 K): δ 42.6 (s, *C*H$_2$), 58.3 (s, O–*C*H$_3$), 71.3 (s, *C*H$_2$), 122.2, 122.7, 128.9 (*o*-, *m*-, *p*-*C*$_6$H$_5$), 129.1, 150.1(*C*$_{ipso}$-*C*$_6$H$_5$ and *C*NN). Anal. Calc. for C$_{20}$H$_{26}$N$_4$O$_2$: C, 67.8; H, 7.4; N, 15.8. Found: C, 67.4; H, 7.3; N, 15.2%.

NMR tube scale reaction of [C$_6$H$_5$N=C{NH(CH$_2$)$_2$OMe}–C{NH(CH$_2$)$_2$OMe}=NC$_6$H$_5$] (1) with benzoic acid. A solution of **1** (10 mg, 0.028 mmol) in $CDCl_3$ (2 ml) in a 5 mm NMR tube was treated with *ca.* 2.0 equiv. of benzoic acid. ^{1}H NMR (400 MHz): δ 3.36 (s, CH_3, 6H), 3.53 (s, CH_2–CH_2, 8H), 6.60–7.18 (m, C$_6$*H*$_5$, 10H, amidine), 7.43 (m, C$_6$*H*$_5$, 4H, benzoate), 7.54 (m, C$_6$*H*$_5$, 2H, benzoate), 8.09 (m, C$_6$*H*$_5$, 4H, benzoate).

[C$_6$H$_5$N=C{NH(CH$_2$)$_2$NMe$_2$}–C{NH(CH$_2$)$_2$NMe$_2$}=NC$_6$H$_5$] (2) (oxam(NMe$_2$)$_2$H$_2$). A yellow solution of [C$_6$H$_5$N=C(Cl)–C(Cl)=NC$_6$H$_5$] (8.3 g, 30 mmol) in toluene (80 ml) was treated with 6.6 ml of *N*,*N*-dimethylethyleneamine (5.3 g, 60 mmol) at 0 °C in a dropwise manner. The reaction mixture was allowed to warm to room temperature and react overnight. After 12 h of stirring, the resulting precipitate was isolated by filtration and pumped to dryness to give a white solid **2**·2HCl. Yield, 10.9 g, 80%. ^{1}H NMR (600 MHz): δ 2.86 (s, CH_3, 12H), 3.29 (s, CH_2, 4H), 3.71 (br, CH_2, 4H), 6.38 (d, *o*-Ph, 4H, *J* = 4.2 Hz), 6.89 (t, *p*-Ph, 2H, *J* = 7.2 Hz), 7.03 (t, *m*-Ph, 4H, *J* = 7.2 Hz).^{13}C{^{1}H} NMR (150 MHz): δ 35.5, 56.7 (s, (*C*H$_2$)$_2$–N), 43.9 (s, N–*C*H$_3$), 121.9, 122.5, 128.1(*o*-, *m*-, *p*-*C*$_6$H$_5$), 148.4, 150.7 (*C*$_{ipso}$-*C*$_6$H$_5$ and *C*NN). The white solid **2**·2HCl (2.2 g, 4.8 mmol) was extracted with CH_2Cl_2 (50 ml), and then treated with 2 ml of $NH_4OH_{(aq)}$ to afford a yellowish-green solution. The resulting solution was filtered and the volatiles were removed *in vacuo* to give compound **2** as an oily solid. Yield, 1.5 g, 81%. The quality is good enough for further reaction. Single crystals suitable for X-ray analysis were grown from hexane at room temperature. ^{1}H NMR (600 MHz, 323K): δ 2.10 (s, CH_3, 12H), 2.24 (s, CH_2, 4H), 3.25 (s, CH_2, 4H), 5.13 (br, N*H*, 2H), 6.75 (br, *o*-Ph, 4H), 6.95 (m, *p*-Ph, 2H), 7.17 (br, *m*-Ph, 4H).^{13}C{^{1}H} NMR (150 MHz, 323 K): δ 38.5 (s, (*C*H$_2$)$_2$–N), 57.3 (s, (*C*H$_2$)$_2$–N), 44.9 (s, N–*C*H$_3$), 121.7, 122.3, 128.5 (*o*-, *m*-, *p*-*C*$_6$H$_5$), 149.3, 151.1 (*C*$_{ipso}$-*C*$_6$H$_5$ and *C*NN). Anal. Calc. for C$_{22}$H$_{32}$N$_6$: C, 69.5; H, 8.4; N, 22.1. Found: C, 68.7; H, 8.9; N, 22.3%.

[(Me$_2$)Al(oxam(OMe)$_2$)Al(Me$_2$)] (3). To a solution of **1** (1.79 g, 5 mmol) in 40 ml of toluene, 5.3 ml of $AlMe_3$ (2 M in toluene, 10.6 mmol) was added dropwise within 5 min at room temperature. The reaction mixture was then set to reflux. After 6 h of stirring, the volatiles were removed under vacuum, and the residue was recrystallized from toluene/hexane to afford a white crystalline solid. Yield, 0.90 g, 37%. ^{1}H NMR (600 MHz): δ −1.02 (s, Al–*C*H$_3$, 12H), 2.89 (t, CH_2, 4H, *J* = 6 Hz), 3.31 (s, O*Me*, 6H), 3.35 (t, CH_2, 4H, *J* = 6 Hz), 7.10 (m, Ph, 4H), 7.12 (m, Ph, 2H), 7.26 (m, Ph, 4H).^{13}C{^{1}H} NMR (150 MHz): δ −11.0 (s, Al–*C*H$_3$), 45.7 (s, (*C*H$_2$)$_2$), 57.9 (s, O–(*C*H$_3$)), 69.6 (s, (*C*H$_2$)$_2$), 124.3, 126.4, 127.8 (*o*-, *m*-, *p*-*C*$_6$H$_5$), 144.6, 155.4(*C*$_{ipso}$-*C*$_6$H$_5$ and *C*NN). Anal. Calc. for C$_{24}$H$_{36}$Al$_2$N$_4$O$_2$: C, 61.8; H, 7.8; N, 12.0. Found: C, 61.6; H, 7.8; N, 11.6%.

[(Me$_2$)Al(oxam(NMe$_2$)$_2$)Al(Me$_2$)] (4). To a solution of **2** (1.8 g, 4.7 mmol) in 40 ml of toluene, a diluted solution of 5 ml of $AlMe_3$ (2 M in toluene, 9.5 mmol) in 80 ml of toluene was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and reacted overnight. After 8 h of stirring, the resulting white solid was isolated by filtration and pumped to dryness. Yield, 1.9 g, 82%. ^{1}H NMR (600 MHz): δ −1.05 (s, Al–*C*H$_3$, 12H), 2.14 (s, N*Me*$_2$, 12H), 2.36 (t, CH_2, 4H, *J* = 6 Hz), 2.72 (t, CH_2, 4H, *J* = 6 Hz), 7.10 (m, Ph, 6H), 7.23 (m, Ph, 4H).^{13}C{^{1}H} NMR (150 MHz): δ −10.0 (s, Al–*C*H$_3$), 43.2 (s, (*C*H$_2$)$_2$–N), 44.5 (s, N–(*C*H$_3$)$_2$), 56.7 (s, (*C*H$_2$)$_2$–N), 123.7, 126.8, 127.4 (*o*-, *m*-, *p*-*C*$_6$H$_5$), 146.3, 155.9 (*C*$_{ipso}$-*C*$_6$H$_5$ and *C*NN). Anal. Calc. for C$_{26}$H$_{42}$Al$_2$N$_6$: C, 63.4; H, 8.6; N, 17.1. Found: C, 62.1; H, 8.4; N, 16.5%.

Table 6 Summary of crystal data for compounds **1**, **2**, **3**, **5** and **6**

	1	**2**	**3**	**5**	**6**
Formula	$C_{23.5}H_{26}N_4O_2$	$C_{44}H_{64}N_{12}$	$C_{12}H_{18}AlN_2O$	$C_{14}H_{20}BrMgN_2O_2$	$C_{15}H_{23}BrMgN_3O$
M	396.48	761.07	233.26	352.54	365.58
T/K	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Orthorhomic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a/Å	9.2839(11)	9.5940(6)	10.3225(10)	9.7976(8)	10.3022(7)
b/Å	11.6924(14)	17.2591(11)	9.2411(8)	11.4638(10)	12.2215(8)
c/Å	11.9217(13)	27.7148(18)	14.5906(13)	15.2253(13)	14.8699(9)
α/°	92.341(3)	90	90	90	90
β/°	112.099(2)	90	108.326(2)	104.651(2)	108.0400(10)
γ/°	106.880(2)	90	90	90	90
V/Å^3	1130.8(2)	4589.1(5)	1321.2(2)	1654.5(2)	1780.2(2)
Z	2	4	4	4	4
ρ_{calc}/Mg m^{-3}	1.164	1.102	1.173	1.415	1.364
μ(Mo-Kα)/mm^{-1}	0.076	0.068	0.136	2.525	2.347
Reflections collected	6486	25891	7182	9070	9764
No. of parameters	265	505	145	181	190
$R1$ [a]	0.0663	0.0688	0.0437	0.0390	0.0360
$wR2$ [a]	0.1748	0.1885	0.1449	0.1154	0.1066
GoF [b]	1.067	1.254	1.113	0.864	0.813

[a] $R1 = [\Sigma(|Fo| - |F_c|)/\Sigma|F_o|]$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = 0.10$. [b] GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

[(Br)(THF)Mg(oxam(OMe)$_2$)Mg(THF)(Br)] (5). To a solution of **1** (0.71 g, 2 mmol) in 40 ml THF, 1.4 ml of MeMgBr (3 M in Et_2O, 4.2 mmol) was added dropwise at 0 °C. The clear yellow solution gradually turns into a pale-yellow suspension. The reaction mixture was allowed to warm to room temperature and was reacted overnight. After 13 h of stirring, the resulting white precipitate was isolated by filtration and pumped to dryness. Yield, 0.91 g, 65%. ^{1}H NMR (200 MHz): δ 1.57 (m, THF, 8H), 2.90 (m, CH_2, 4H), 3.44 (m, CH_2, 4H), 3.48 (s, O–CH_3, 6H), 3.69 (m, THF, 8H), 6.88–7.20 (m, Ph, 10H).^{13}C{^{1}H} NMR (150 MHz): δ 25.0(s, *THF*), 46.5 (s, (*C*H$_2$)$_2$), 58.9 (s, O–(*C*H$_3$)), 69.2 (s,*THF*), 73.3 (s, (*C*H$_2$)$_2$), 124.3, 126.4, 127.8 (*o*-, *m*-, *p*-*C*$_6$H$_5$), 144.6, 155.4 (*C*$_{ipso}$-*C*$_6$H$_5$ and *C*NN). Anal. Calc. for $C_{28}H_{40}Br_2Mg_2N_4O_4$: C, 47.7; H, 5.7; N, 8.0. Found: C, 47.4; H, 5.5; N, 8.0%.

[(Br)(THF)Mg(oxam(NMe$_2$)$_2$)Mg(THF)(Br)] (6). To a solution of **2** (1.4 g, 3.6 mmol) in 30 ml of THF, a diluted solution of 2.4 ml of MeMgBr (3 M in Et_2O, 7.2 mmol) in 30 ml of THF was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and reacted for 3 h. The resulting white solid was isolated by filtration and pumped to dryness. Yield, 2.1 g, 80%. ^{1}H NMR (200 MHz): δ 1.61 (m, THF, 8H), 2.27 (m, CH_2 and N–(CH_3)$_2$, overlap, 10H), 2.74 (m, CH_2, 4H), 3.75 (m, THF, 8H), 6.88–7.17 (m, Ph, 10H).^{13}C{^{1}H} NMR (75 MHz): δ 25.1 (s, *THF*), 44.4 (s, (*C*H$_2$)$_2$), 45.1 (s, N–(*C*H$_3$)$_2$), 60.3 (s, (*C*H$_2$)$_2$), 69.2 (s, *THF*), 120.6, 125.2, 127.3 (*o, m, p*-*C*$_6$H$_5$), 150.2, 160.9 (*C*$_{ipso}$-*C*$_6$H$_5$ and *C*NN). Anal. Calc. for $C_{30}H_{46}$ $Br_2Mg_2N_6O_2$: C, 49.3; H, 6.3; N, 11.5. Found: C, 49.1; H, 6.2; N, 11.3%.

Crystal structure data

Crystals were grown from toluene/hexane solution (**1**), concentrated hexane solution (**2**), dichloromethane/hexane solution (**3**), THF/hexane solution (**5**), or dichloromethane/hexane solution (**6**), and isolated by filtration. Suitable crystals of **1**, **2**, **3**, **5** and **6** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using the SADABS program.[56] The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package.[57] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Some details of the data collection and refinement are given in Table 6.

CCDC reference numbers 203776–203780.

See http://www.rsc.org/suppdata/dt/b3/b301744c/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We would like to thank the National Science Council of the Republic of China for financial support.

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