

Magnesium, zinc and aluminium complexes supported by tripodal diaminebis(aryloxydo) ligands: synthesis, solid state and solution structure†

Ewa Kober, Zofia Janas,* Tomasz Nerkowski and Lucjan B. Jerzykiewicz

Cite this: *Dalton Trans.*, 2013, **42**, 10847

The reactions of the diaminebis(aryloxydo) ligand precursors $[\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{-4-R-C}_6\text{H}_3\text{OH})_2]$ $[\text{R} = \text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3, \text{H}_2\text{L}^1; \text{R} = \text{CH}_3, \text{H}_2\text{L}^2]$ with Mg^nBu_2 , ZnEt_2 and AlEt_3 create complexes of general formula $[\text{M}_2(\mu\text{-L-}\kappa^4\text{O,N,N,O})_2]$ ($\text{M} = \text{Mg}$, **1a** for L^1 and **1b** for L^2 ; $\text{M} = \text{Zn}$, **2a** for L^1 and **2b** for L^2) and $[\text{Al}_2(\mu\text{-L-}\kappa^3\text{O,N,N,O})_2\text{Et}_2]$ (**3** for L^1) in good yields. Compounds **1a–3** were characterized by NMR spectroscopy and ESI-MS experiments. The definitive molecular structure of **1b**· CH_2Cl_2 , **2a**· H_2O , **2b**· CH_2Cl_2 and **3** was provided by a single-crystal analysis and revealed their dimeric nature with an M_2O_2 planar core. The L^1 and L^2 ligands coordinate as the dianions in a tetradentate/bridging manner in **1b**, **2a**, **2b** and in a tridentate/bridging mode in **3**. The NMR spectra showed that the solid state of these compounds is essentially retained in solution.

Received 9th April 2013,
Accepted 28th May 2013

DOI: 10.1039/c3dt50938a

www.rsc.org/dalton

Introduction

Polydentate diaminebis(aryloxydo) (ONNO) ligands have been used extensively in transition metal coordination chemistry for catalyst development,^{1,2} metalloenzyme mimicry,^{1,3} and cytotoxicity against particular cells^{1,4} as well as magnetic studies.⁵ The broad application range arises from the great modification possibilities either on the phenyl group or the amine one leading to the convenient variation of steric factors and donor ability of those class ligands.

A particularly convenient method for the synthesis of transition metal complexes supported by diaminebis(aryloxydo) ligands is through a metathesis route that often involves main group metal derivatives *e.g.*, Li, Na, Mg, Ca, Al as well as Zn compounds.⁶ Although the zinc ion has filled d-orbitals but shows many similar properties to magnesium including a similar ionic radius, complexes of these two metals are studied together. To fully exploit this method, it is necessary to identify the structure of starting materials. Up to date, only a few lithium compounds of the general formula $[\text{Li}_2(\text{ONNO})]$ with diaminebis(aryloxydo) ligands have been fully characterized.⁷ Also only a few alkaline earth metal complexes of the tripodal diaminebis(aryloxydo) ligands have been reported. For the magnesium complex the four-coordinate, mononuclear structure is postulated based on the NMR studies while the

dinuclear calcium compound with formally the hexa-coordinate environment around metal ions, both in the solid state and in solution, is well documented.⁸ The monomeric nature in the solid state of the zinc complexes having a four- or five-coordinate environment (depending on solvent coordination) has been established for either $[\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{-2,4-}^t\text{Bu}_2\text{-C}_6\text{H}_2\text{O})_2]^{2-}$ or $[\text{Me}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{-2-}^t\text{Bu-4-Me-C}_6\text{H}_3\text{O})_2]^{2-}$ ligands.⁹ However, the asymmetrical tripodal diaminebis(aryloxydo) ligands, $[(\text{C}_5\text{H}_5\text{N})\text{CH}_2\text{CH}_2\text{N}\{(\text{CH}_2\text{-2-}^t\text{Bu-4-Me-C}_6\text{H}_2\text{O})\text{-(CH}_2\text{-C}_6\text{H}_4\text{O})\}]^{2-}$ and $[(\text{C}_5\text{H}_5\text{N})\text{CH}_2\text{CH}_2\text{N}\{(\text{CH}_2\text{-2-}^t\text{Bu-4-OMe-C}_6\text{H}_2\text{O})\text{-(CH}_2\text{-C}_6\text{H}_4\text{O})\}]^{2-}$, generate dimeric zinc complexes containing a five-coordinate environment around each metal centre.^{5b,e} In contrast, only monomeric aluminium complexes have been published which depending upon the steric properties of the phenoxy substituents and steric hindrance at the amine side-chain have different coordination geometries in the solid state either (distorted) trigonal bipyramidal or square planar.¹⁰ In addition to having various, interesting structural motifs, some of the Li, Mg, Zn and Al compounds based on the diaminebis(aryloxydo) ligands have also been shown to be efficient initiators for the ring-opening polymerization (ROP) of cyclic esters such as lactide and ϵ -lactone.^{8,10,11}

Following our recently reported work on the tripodal diaminebis(aryloxydo) ligands shown in Fig. 1, which generate declivable lithium structures compared to their *ortho* and *para* substituted derivatives,^{7d} we decided to examine how a lack of the substituent in the *ortho*-position on two phenoxy rings influences the structures of related Mg, Zn and Al complexes in the solid state and in solution.

Faculty of Chemistry, University of Wrocław, 14, F. Joliot-Curie, 50-383 Wrocław, Poland. E-mail: zofia.janas@chem.uni.wroc.pl

†CCDC 932554, 874666, 876629, 874667 and 876628. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50938a

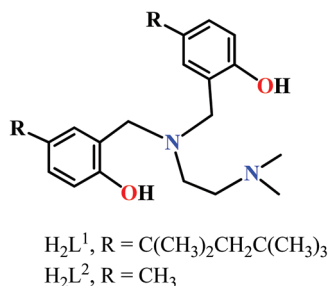


Fig. 1 Tetradentate diaminebis(aryloxy) ligand precursors.

Herein, we report the synthesis and structural characterization of new Mg, Zn and Al complexes based on the ligand precursors presented in Fig. 1.

Results and discussion

We previously reported the preparation of the ligand precursors H_2L^1 and H_2L^2 (Fig. 1).^{7d} They were synthesized in a similar way, *via* the straightforward, single-step Mannich condensation between *N,N*-dimethylethylenediamine, paraformaldehyde and 4-(1,1,3,3-tetramethylbutyl)phenol or *p*-cresol, respectively in a 1 : 2 : 2 molar ratio in MeOH or EtOH.^{7d} The ligand precursors were identified by NMR, ESI-MS and elemental analysis and the definitive molecular structure of H_2L^2 was provided by a single-crystal analysis. However, only qualitative information was extracted for H_2L^1 because of the insufficient quality of the crystal.^{7d} Finally, recrystallization of H_2L^1 from the mixture of thf-MeOH (1 : 1) gave colourless crystals suitable for the X-ray structure determination. The crystal of H_2L^1 contains two independent molecules in the asymmetric unit and in Fig. 2 the molecular structure of the molecule (A) is shown. The selected parameters including hydrogen bond lengths and angles are given in the caption. The structure revealed the evidence for three intramolecular hydrogen-bond interactions between O11A–H11A...N12A [2.759(6) Å, 148°], O12A–H12A...N11A

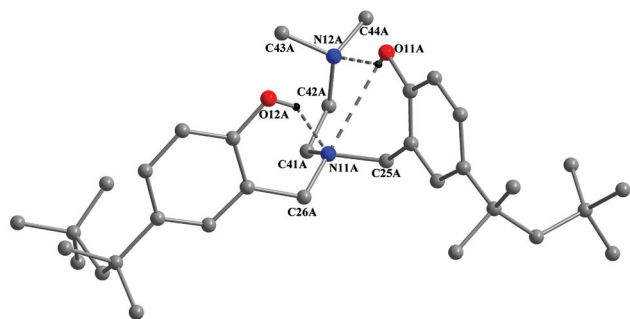


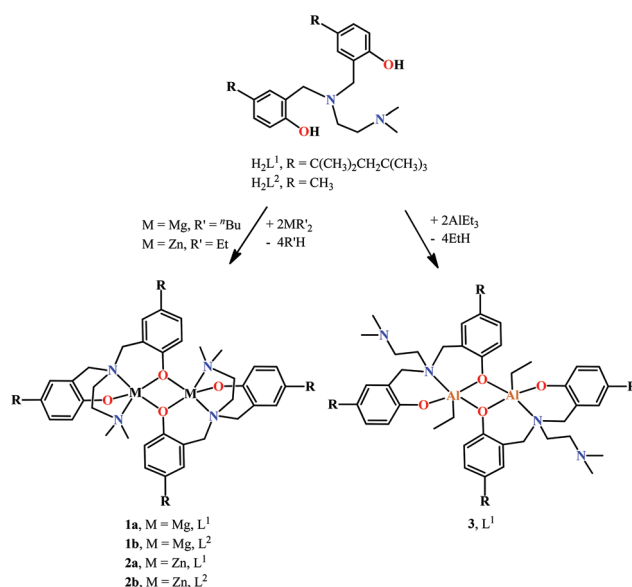
Fig. 2 The molecular structure of H_2L^1 . Only one molecule (A) is shown for clarity. Hydrogen atoms except those involving in hydrogen bond-interactions are omitted. Selected parameters (bonds, Å; angles, °): N11A–C25A 1.480(7), N11A–C26A 1.460(6), N11A–C41A 1.478(6), N12A–C43A 1.467(7), N12A–C44A 1.466(7), N12A–C42A 1.469(6), C41A–C42A 1.514(7), O11A–H11A...N12A 2.759(6), O12A–H12A...N11A 2.720(5), O11A–H11A...N11A 3.114(5), O11A–H11A...N12A 148, O12A–H12A...N11A 146, O11A–H11A...N11A 120.

[2.720(5) Å, 146°] and O11A–H11A...N11A [3.114(5) Å, 120°], which may contribute to the tripodal configuration that adopts the molecule framework. The same structural feature was observed for the di-Mannich base containing *ortho* and *para* substituents on the phenolic rings.^{2c} Furthermore, weak C–H...O interactions [3.384(6)–3.516(6) Å, 164–170°] stabilize the crystal packing, building a three-dimensional network.

Key reactions to generate magnesium, zinc and aluminium series based on the L^1 and L^2 ligands are shown in Scheme 1 and are based on the σ -bond metathesis reaction between the ligand precursors and appropriate homoleptic metal alkyls. Complexes $[\text{M}_2(\mu\text{-L-}\kappa^4\text{O,N,N,O})_2]$ ($\text{M} = \text{Mg}$, **1a** for L^1 and **1b** for L^2 ; $\text{M} = \text{Zn}$, **2a** for L^1 and **2b** for L^2) and $[\text{Al}_2(\mu\text{-L-}\kappa^3\text{O,N,N,O})_2\text{Et}_2]$ (**3** for L^1), were synthesized by the straightforward reactions of Mg^nBu_2 , ZnEt_2 and AlEt_3 , respectively, with the ligand precursors H_2L^1 or H_2L^2 in thf or *n*-hexane. Unfortunately, attempts to isolate a chemically pure aluminium compound with an L^2 ligand failed.

Compounds **1a–3** were fully characterized by analytical and spectroscopic methods. The ESI-MS spectrometry was recorded as representative for characterization. The molecular ion peaks appeared at m/z : 1093.8 [**1a** + H]⁺, 701.4 [**1b** + H]⁺, 1173.7 [**2a** + H]⁺, 781.2 [**2b** + H]⁺, 1157.9 [**3** + H]⁺. For **1b**, **2a**, **2b** and **3**, X-ray single-crystal diffraction studies were essential to unveil the nuclearity in the solid state.

As illustrated in Fig. 3–5, complexes **1b**· CH_2Cl_2 , **2a**· H_2O , **2b**· CH_2Cl_2 and **3** have a dimeric character with an M_2O_2 planar core. The L^1 and L^2 ligands coordinate as the dianions (all the hydroxyl groups are deprotonated) in a tetradentate/bridging manner in **1b**· CH_2Cl_2 , **2a**· H_2O and **2b**· CH_2Cl_2 , specifically through two aryloxy oxygen atoms and two nitrogen atoms of the diamine group. However, in the case of **3** a tridentate/bridging mode of the L^1 ligand, through two aryloxy oxygen atoms and the tripodal nitrogen atom of the diamine group, is revealed. The metal centres in each complex adopt the five-



Scheme 1 Synthetic strategy of complexes **1a–3**.



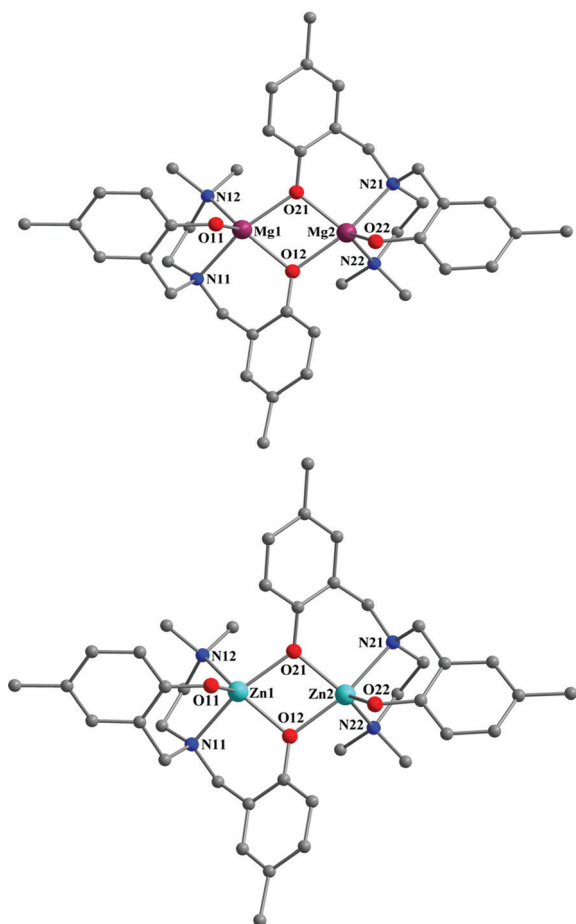


Fig. 3 Molecular structures of **1b**-CH₂Cl₂ (top) and **2b**-CH₂Cl₂ (bottom). Hydrogen atoms and the CH₂Cl₂ solvent species are omitted for clarity. Selected parameters (bonds, Å; angles, °) for **1b**: Mg1...Mg2 3.063(1), Mg1-O11 1.916(2), Mg1-O12 1.997(2), Mg1-O21 2.005(2), Mg1-N11 2.235(2), Mg1-N12 2.247(2), Mg2-O22 1.925(2), Mg2-O21 1.971(2), Mg2-O12 2.006(2), Mg2-N22 2.219(2), Mg2-N21 2.230(2), O11-Mg1-O12 112.38(7), O11-Mg1-N11 92.72(6), O21-Mg1-N11 156.32(6), N11-Mg1-N12 79.45(6), O22-Mg2-O21 118.89(6), O22-Mg2-N22 115.13(8), O21-Mg2-N21 89.94(6), O12-Mg2-N21 162.07(7), N22-Mg2-N21 80.20(6); for **2b**: Zn1...Zn2 3.159(1), Zn1-O11 1.928(1), Zn1-O12 2.024(1), Zn1-O21 2.039(1), Zn1-N12 2.185(3), Zn1-N11 2.193(3), Zn2-O22 1.934(1), Zn2-O21 1.998(2), Zn2-O12 2.047(2), Zn2-N22 2.152(3), Zn2-N21 2.195(3), O11-Zn1-O12 110.61(5), O11-Zn1-N11 94.72(6), O21-Zn1-N11 155.73(6), N12-Zn1-N11 81.21(6), O22-Zn2-O12 104.03(5), O22-Zn2-N22 117.44(6), N22-Zn2-N21 82.11(6).

coordinate geometry with the τ values of 0.35 for Mg1 and 0.61 for Mg2 in **1b**; 0.56 for Zn1 and Zn2 in **2a**; 0.35 for Zn1 and 0.62 for Zn2 in **2b**; 0.69 for both Al atoms in **3**. On the basis of the τ values the coordination geometry around the metal centres in these compounds lies between a regular square pyramid (sqp) and a regular trigonal bipyramid (tbp).¹² Nevertheless, the values of the O-M-N, O-M-O and N-M-N angles appear more appropriate for the tbp geometry and the geometry adopted by metal atoms can be accepted as a distorted trigonal bipyramid. In all structures the bridging aryloxy oxygen and the tripodal nitrogen of the L ligand coordinate in the axial positions while the remainder bound donor atoms are situated in the equatorial sites.

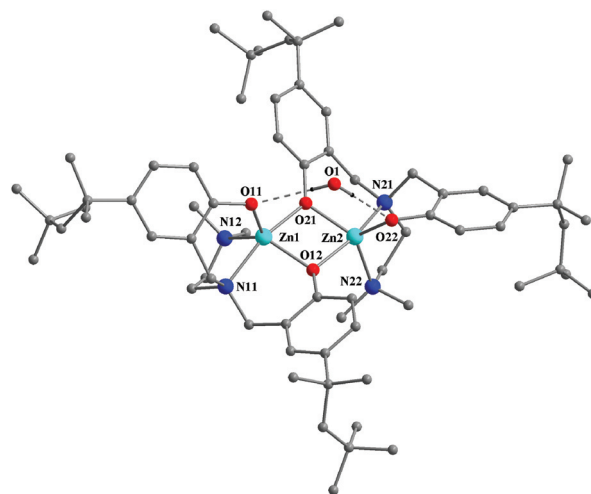


Fig. 4 Molecular structure of **2a**-H₂O. Hydrogen atoms except those involved in hydrogen bond-interactions are omitted for clarity. Selected parameters (bonds, Å; angles, °): Zn1...Zn2 3.160(1), Zn1-O11 1.941(2), Zn1-O12 2.001(2), Zn1-O21 2.057(2), Zn1-N11 2.201(2), Zn1-N12 2.145(2), Zn2-O12 2.065(2), Zn2-O21 1.996(2), Zn2-O22 1.947(2), Zn2-N21 2.180(2), Zn2-N22 2.143(2), O11-Zn1-O12 114.10(8), O11-Zn1-N11 93.60(8), O21-Zn1-N11 163.17(8), N11-Zn1-N12 82.58(9), O21-Zn2-O22 115.16(8), O12-Zn2-N21 161.76(8), N21-Zn2-N22 83.53(9), O1-H11...O11 2.960(3), O1-H12...O22 2.853(3), O1-H11...O11 162, O1-H12...O22 177.

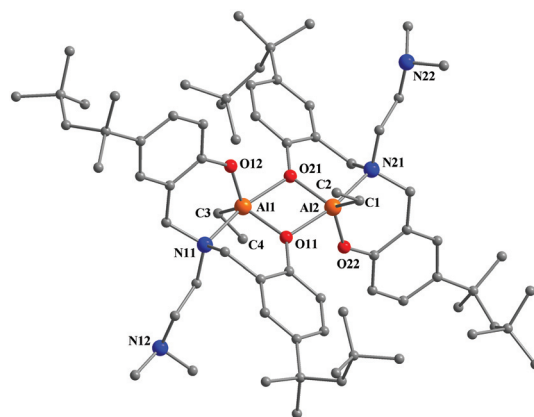


Fig. 5 Molecular structure of **3**. Hydrogen atoms are omitted for clarity. Selected parameters (bonds, Å; angles, °): Al1...Al2 3.008(4), Al1-O11 1.843(2), Al1-O12 1.766(2), Al1-O21 1.995(2), Al1-N11 2.118(3), Al2-O11 1.978(2), Al2-O21 1.833(2), Al2-O22 1.767(2), Al2-N21 2.131(3), O11-Al1-O12 116.01(11), O11-Al1-N11 89.34(10), O21-Al1-N11 163.82(10), O21-Al2-O2 114.68(11), O11-Al2-N21 88.83(11), O21-Al2-N21 164.02(11).

The molecular structures of **1b**-CH₂Cl₂ and **2b**-CH₂Cl₂ with selected bond lengths and angles are shown in Fig. 3. The terminal Mg-O bond lengths of 1.916(2) and 1.925(2) Å fall in the usual range, and are as expected substantially shorter than the bridging Mg-μ-O distances of 1.995 Å (av.).¹³ However, while the three of the Mg-μ-O bond lengths are very similar [1.997(2), 2.005(2) and 2.006(2) Å], the fourth one (Mg2-O21) is significantly shorter by 0.03 Å. Furthermore, the values of the Mg-N distances are statistically similar (within 3 σ range) although the tripodal nitrogen atom and that of the pendant



arm in the L ligands differ in their electronic properties and in consequence, in the donor abilities. However, the similarity in the M–N distances in **1b**·CH₂Cl₂ is not unusual and has been observed in the related five-coordinate zinc and cobalt complexes^{5a,b,e,9} as well as in the monomeric six-coordinate vanadium(v) compounds.³ The same trend in bond parameters applies to **2b**·CH₂Cl₂ (Fig. 3), which is virtually isostructural to **1b**·CH₂Cl₂ and a direct comparison of the M–O and M–N distances and angles is possible for the central N₄M₂O₄ skeletons. It is worth noting that the M–O(terminal) bond lengths [Zn–O, 1.928(1) and 1.934(1) Å] are closely matched in these two molecules according to similar ionic radii of Mg²⁺ and Zn²⁺, though the Zn–N distances are significantly shorter by 0.05 Å. However the Zn–μ-O distances are notably longer by 0.03 Å than the corresponding Mg–μ-O distances in **1b**·CH₂Cl₂, in part, it must be a reflection of the different M···M separation [Mg···Mg, 3.063(1) Å; Zn···Zn, 3.159(1) Å]. To our knowledge, complex **1b**·CH₂Cl₂ is the first crystallographically characterized example of a magnesium compound bearing the diaminebis(aryloxido) ligand.

In contrast to **1b**·CH₂Cl₂ and **2b**·CH₂Cl₂, compound **2a** crystallizes with H₂O as a solvate molecule (Fig. 4). Solvating character of H₂O in **2a**·H₂O was confirmed by successful refinements of two hydrogen bonds O1–H11···O11 and O1–H12···O22 implicated by the distances of 2.960(3) and 2.853(3) Å with the angles of 162 and 177°, respectively, that are close to linear (180°). It is clearly noticeable in the structure of **2a**·H₂O that the presence of the hydrogen bond interaction plays an important role in the differences between the two moieties of the dimer. In contrast to **1b**·CH₂Cl₂ and **2b**·CH₂Cl₂, both Zn atoms in **2a**·H₂O have identical τ values and in consequence the same distortion from ideal t_{bp} geometry. The Zn–O(terminal) bond lengths of 1.941(2) and 1.947(2) Å are slightly longer than the corresponding distances in **2b**·CH₂Cl₂ as a result of participation of O11 and O22 in the H-bonding with the H₂O molecule. However, neither of these distances fall outside the range of the Zn–O distances observed in other five-coordinate aryloxide Zn(II) complexes [1.931–1.961 Å].^{5a,b,e,9,14} The bridge between Zn1 and Zn2 atoms formed by two oxygen atoms of the L¹ ligand in **2a**·H₂O is asymmetric, (Zn1–O12) 2.001(2) Å and (Zn1–O21) 2.057(2) Å and the two zinc(II) centres are separated by 3.160(1) Å. Interestingly, the Zn–N(tripodal) distances of 2.201(2) and 2.180(2) Å are significantly longer than the Zn–N(dimethyl sidearm) [2.145(2) and 2.143(2) Å] but very similar to those in **2b**·CH₂Cl₂.

It is worthwhile underlining that the diaminebis(aryloxido) ligand having *tert*-butyl substituents in both *ortho* and *para* positions on two phenoxo rings creates monomeric four-coordinate magnesium and zinc complexes.⁸ The single-crystal analysis of Zn derivatives showed to have a distorted trigonal-bipyramidal arrangement around the zinc centre formed by the donor atoms of the [Me₂NCH₂CH₂N(CH₂-2,4-*t*Bu₂-C₆H₂O)₂]^{2–} ligand.⁹ This four-coordinate Zn complex after coordination with the tetrahydrofuran molecule forms a five-coordinate trigonal-bipyramidal complex.^{6b} However, the less bulky [(C₅H₅N)CH₂CH₂N{[(CH₂-2-*t*Bu-4-R-C₆H₂O)(CH₂-C₆H₄O)]^{2–}

(R = Me, OMe) ligands containing one unsubstituted phenoxo ring and the second one with *ortho* and *para* substituent groups generate the dimeric zinc complexes in which the unsubstituted phenolate oxygen provides bridging coordination and the geometry around the two Zn ions is distorted trigonal bipyramid like in compounds **1a–2b**.^{5e}

The molecular structure of [Al₂(μ-L-κ³O,N,N,O)₂Et₂] (**3**) with selected bond lengths and angles is shown in Fig. 5. The Al–O bond lengths range from 1.766(2) to 1.995(2) Å, as expected the bridging is longer than the terminal, and are similar to those found in other structures of the five-coordinate aluminium aryloxides.^{10,15} The Al–C distances of 1.976(3) and 1.960(3) Å are compatible with those found in the organo-aluminium aryloxides.^{10b,15a,b,d-f,h,16} The Al–N bond lengths of 2.118(3) and 2.131(3) Å are similar to the Al–N(tripodal) distances [2.1083(13) and 2.153(2) Å] for monomeric, five-coordinate complexes [Al(L-κ⁴O,N,N,O)(OⁱPr)] [L = {Me₂NCH₂CH₂N(CH₂-2-*t*Bu-4-OMe-C₆H₂O)₂}^{2–} or {Me₂NCH₂CH₂N(CH₂-2-*t*Bu-4-Br-C₆H₂O)₂}^{2–}] and markedly shorter than the corresponding distances found for [Al(L-κ⁴O,N,N,O)X] [L = Me₂NCH₂CH₂N(CH₂-2,4-*t*Bu₂-C₆H₂O)₂}^{2–}; X = Me, OBn] [2.2150(16) and 2.186(4) Å].^{10a,b} For comparison, the Al–N(tripodal) distances in the alkoxide bridged dimer [Al₂(μ-L-κ⁴O,N,N,O)₂] [L = {OCH₂CH₂N(CH₂-2,4-Me₂-C₆H₂O)₂}^{3–}] [2.094(1) and 2.066(1) Å] are shorter than the corresponding distances in **3**.¹⁴ Particularly noteworthy in the structure of **3** is the non-coordination mode of the nitrogen sidearm. Complex **3** as a dimer is the first example among aluminium complexes bearing the diaminebis(aryloxido) ligands. In contrast to **3**, the diaminebis(aryloxido) ligands having the *tert*-butyl substituents in both *ortho* and *para* or the *tert*-butyl in *ortho* and the methyl in *para* positions of the phenoxo groups with the same CH₂CH₂NMe₂ as well as the different amine side-chains of the ligand included CH₂CH₂NEt₂ or pyridine create solely monomeric aluminium complexes having the trigonal-bipyramidal or square-pyramidal geometry around the metal center.¹⁰

The question of whether **1b**, **2a**, **2b** and **3** which, by X-ray crystallography, are dimeric with five-coordinate metal centres in the solid state, remain dimeric or cleave into four- (**1b**, **2a**, **2b**) or five-coordinate (in the case of **3**) monomers in solution was addressed through variable-temperature (VT) ¹H NMR measurements. According to the X-ray structures, the C₁-symmetric **1b**, **2a**, **2b** and **3** should have four signals for the methylene protons of the ArCH₂N– units at room temperature. Thus, the NMR spin system of ArCH₂N– for **1b**, **2a**, **2b** and **3** will be AB due to their symmetry. In fact, at room temperature the proton spectra of **1b**, **2a**, **2b** in CDCl₃ and **3** in C₆D₅CD₃ exhibit four sharp doublets for the protons of the ArCH₂N– unit (δ 4.34, 4.06, 2.86, 2.65 for **1b**; 4.47, 4.28, 3.03, 2.74 for **2a**; 4.57, 4.42, 3.92, 3.08 for **3**; ²J = 11.8–13.8 Hz). Also four multiplets for the methylene protons of the –NCH₂CH₂N– group (δ 3.78, 3.09, 2.92, 2.43 for **1b**; 3.11, 2.89, 2.19, 2.11 for **2a**) reflect the NMR spin system AA'BB' for **1b**, **2a** and **2b**. The same pattern of resonances appears for **1a** indicating an analogous structure to **1b**. However, in the case of **3**, the –NCH₂CH₂N– group demonstrates one multiplet and one triplet in



accordance with the solid state structure. Likewise, double signals for the rest of the protons of the L^1 and CH_3CH_2 ligands are observed except the magnetically equivalent methyl protons of the sidearm NMe_2 in **3** (δ 1.77 ppm, similarly as in the ligand precursor H_2L^1 δ 1.99 ppm). Furthermore, the VT 1H NMR analysis of **1a–3** does not show any significant differences (in $CDCl_3$ or $C_6D_5CD_3$ from 233 K to 313 K), suggesting that the solid state of these compounds is essentially retained in solution within the temperature range studied.

In conclusion, a family of the diaminebis(aryloxo) magnesium, zinc and aluminium complexes **1a–3** of the tetradentate dianionic (ONNO) ligands, comprising different substituents at a position *para* to the phenolic oxygen atom, $C(CH_3)_2CH_2C(CH_3)_3$ in L^1 and CH_3 in L^2 have been prepared in good yields. Their structures have been characterized in solution by NMR spectroscopy and in the solid state by X-ray determination except for **1a** allowing us to find that these substituents do not cause a remarkable change in the metal coordination geometry. The molecular structures of **1b**· CH_2Cl_2 , **2a**· H_2O , **2b**· CH_2Cl_2 and **3** revealed that the lack of a substituent at the *ortho* position to the phenolic oxygen atom in the ligands L^1 and L^2 resulted in the creation of distinctly different coordination geometry around metal centres than their analogues containing both *ortho* and *para* substituents, reported in the literature. Furthermore, the NMR studies showed that the solid states of the described compounds are essentially retained in solution.

The knowledge of the structures of the diaminebis(aryloxo) magnesium and zinc complexes described here allowed us to explore the synthetic methodology for the preparation of heterometallic vanadium complexes, which are currently underway in our laboratory. Additionally, such well-defined complexes which remain in their solid state structure also in solution can be used as the potential initiators for the ROP of cyclic esters.

Experimental section

General remarks

All operations were carried out under a dry dinitrogen atmosphere, using standard Schlenk techniques. All the solvents were distilled under dinitrogen from the appropriate drying agents prior to use. Reagents were purchased from the Aldrich Chemical Co. and used without further purification unless stated otherwise. The ligand precursors H_2L^1 and H_2L^2 were prepared by a Mannich condensation following literature procedures.^{7d} NMR spectra were performed on a Bruker ARX 500 spectrometer. The electrospray mass spectra (ESI-MS) were recorded on a Bruker MicroTOF-Q mass spectrograph. Microanalyses were conducted on a Vario EL III CHNS Elemental Analyzer (in-house).

Synthesis of $[Mg_2(\mu-L^1-\kappa^4O,N,N,O)_2](1a)$

To an ice cold solution of H_2L^1 (1.20 g, 2.28 mmol) in thf (20 cm^3) was added slowly $Mg^{n}Bu_2$ (2.3 cm^3 , 1 M in heptane, 2.28 mmol). The mixture was stirred for 10 minutes and then

was allowed to reach room temperature. After stirring for 12 h at room temperature volatile materials were removed under vacuum to yield a white powder (1.1 g, 88.0%). Anal. Calcd for $C_{68}H_{108}N_4O_4Mg_2$: C, 74.67; H, 9.96; N, 5.13. Found: C, 74.60; H, 9.92; N, 5.13. 1H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.89–6.55 (m, 12H, C_6H_3); 4.32 (d, $^2J = 12.0$ Hz, 2H, $ArCH_2N$); 4.12 (d, $^2J = 12.5$ Hz, 2H, $ArCH_2N$); 3.11 [m, 2H, $NCH_2CH_2N(CH_3)_2$]; 2.93 (d, $^2J = 12.0$ Hz, 2H, $ArCH_2N$); 2.69 (d, $^2J = 12.5$ Hz, 2H, $ArCH_2N$); 2.56, 2.01 [m, 2H $NCH_2CH_2N(CH_3)_2$]; 1.97, 1.94 [s, 6H, $N(CH_3)_2$]; 1.84 [m, 2H, $NCH_2CH_2N(CH_3)_2$]; 1.66, 1.62 [s, 4H, $C(CH_3)_2CH_2C(CH_3)_3$]; 1.35, 1.30 [s, 12H, $C(CH_3)_2CH_2C(CH_3)_3$]; 0.71, 0.67 [s, 18H, $C(CH_3)_2CH_2C(CH_3)_3$]. ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 158.5, 154.6, 140.7, 138.5, 129.6, 129.0, 128.4, 128.1, 122.2, 121.0, 119.3, 116.4 (C_6H_3); 60.7, 59.7 ($ArCH_2N$); 57.9, 57.6 [$C(CH_3)_2CH_2C(CH_3)_3$]; 56.3 [$NCH_2CH_2N(CH_3)_2$]; 50.5 [$NCH_2CH_2N(CH_3)_2$]; 45.3, 44.8 [$N(CH_3)_2$]; 37.7, 38.0 [$C(CH_3)_2CH_2C(CH_3)_3$]; 33.0, 32.6 [$C(CH_3)_2CH_2C(CH_3)_3$]; 32.4, 32.0 [$C(CH_3)_2CH_2C(CH_3)_3$]; 31.8, 31.5 [$C(CH_3)_2CH_2C(CH_3)_3$]. ESI-MS: m/z : 1093.8 [**1a** + H] $^+$.

Synthesis of $[Mg_2(\mu-L^2-\kappa^4O,N,N,O)_2]\cdot CH_2Cl_2$ (**1b**· CH_2Cl_2)

Compound **1b** was prepared by an analogous procedure to that employed for **1a**, but using H_2L^2 (0.98 g, 2.98 mmol), thf (20 cm^3) and $Mg^{n}Bu_2$ (3.0 cm^3 , 1.0 M solution in heptane, 3.00 mmol) (0.98 g, 84.4%). The crude product was recrystallized from saturated solution in CH_2Cl_2 to give colourless crystals of **1b**· CH_2Cl_2 suitable for the X-ray structure determination. Anal. Calcd for $C_{41}H_{54}Cl_2N_4O_4Mg_2$: C, 62.73; H, 6.94; Cl, 8.92; N, 7.14. Found: C, 62.66; H, 6.93; Cl, 8.90; N, 7.14. 1H NMR (500 MHz, $CDCl_3$, 298 K): δ 7.92–6.54 (12H, C_6H_3); 5.30 (s, 2H, CH_2Cl_2); 4.34 (d, $^2J = 11.9$ Hz, 2H, $ArCH_2N$); 4.06 (d, $^2J = 12.5$ Hz, 2H, $ArCH_2N$); 3.78 [m, 2H, $NCH_2CH_2N(CH_3)_2$]; 3.09 [m, 2H, $NCH_2CH_2N(CH_3)_2$]; 2.92 [m, 2H, $NCH_2CH_2N(CH_3)_2$]; 2.86 (d, $^2J = 12.0$ Hz, 2H, $ArCH_2N$); 2.65 (d, $^2J = 12.5$ Hz, 2H, $ArCH_2N$); 2.43 [m, 2H, $NCH_2CH_2N(CH_3)_2$]; 2.20, 2.17 [s, 6H, $N(CH_3)_2$]; 2.05, 1.99 (s, 6H, $ArCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ 164.2, 158.6, 131.7, 131.3, 130.9, 130.5, 130.1, 128.3, 122.7, 121.6, 120.0, 117.0 (C_6H_3); 59.9, 59.4 ($ArCH_2N$); 57.9 [$NCH_2CH_2N(CH_3)_2$]; 53.8 (CH_2Cl_2); 50.1 [$NCH_2CH_2N(CH_3)_2$]; 45.2, 45.0 [$N(CH_3)_2$]; 20.7, 20.4 ($ArCH_3$). ESI-MS: m/z : 701.4 [**1b** + H] $^+$.

Synthesis of $[Zn_2(\mu-L^1-\kappa^4O,N,N,O)_2]\cdot H_2O$ (**2a**· H_2O)

Compound **2a** was prepared by an analogous procedure to that employed for magnesium compounds, but using H_2L^1 (2.00 g, 3.90 mmol), and $ZnEt_2$ (3.9 cm^3 , 1.0 M in *n*-hexane, 3.90 mmol), *n*-hexane (30 cm^3). The product was precipitated as a white powder (1.90 g, 86.5%). Crystals suitable for the X-ray structure determination as **2a**· H_2O were obtained from CH_2Cl_2 – CH_3CN (1 : 1) solution upon storing in a refrigerator for a few weeks. Anal. Calcd for $C_{68}H_{110}N_4O_5Zn_2$: C, 68.53; H, 9.31; N, 4.70. Found: C, 68.48; H, 9.29; N, 4.65. 1H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.01–6.65 (m, 12H, C_6H_3); 6.74 (br, s, 2H, H_2O); 4.47 (d, $^2J = 11.8$ Hz, 2H, $ArCH_2N$); 4.28 (d, $^2J = 12.2$ Hz, 2H, $ArCH_2N$); 3.11 [m, 2H, $NCH_2CH_2N(CH_3)_2$]; 3.03 (d, $^2J = 11.8$ Hz, 2H, $ArCH_2N$); 2.89 [m, 2H, $NCH_2CH_2N(CH_3)_2$];



2.74 (d, $^2J = 12.3$ Hz, 2H, ArCH_2N); 2.19, 2.11 [m, 2H, $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$]; 1.86, 1.83 [s, 6H, $\text{N}(\text{CH}_3)_2$]; 1.67, 1.64 [s, 4H, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 1.35, 1.32 [s, 12H, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 0.71, 0.69 [s, 18H, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]. ^{13}C NMR (125 MHz, CDCl_3 , 298 K): δ 156.3, 155.4, 145.6, 144.1, 128.7, 127.9, 123.4, 122.2, 120.2, 119.6, 118.2, 116.4 (C_6H_3); 61.7, 59.5 (ArCH_2N); 58.2 [$\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$]; 57.5, 57.2 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 49.6 [$\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$]; 46.5, 45.6 [$\text{N}(\text{CH}_3)_2$]; 37.9, 37.6 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 32.7, 32.4 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 32.4, 32.2 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 32.0, 31.5 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]. ESI-MS: m/z : 1173.7 [$2\mathbf{a} + \text{H}$] $^+$.

Synthesis of $[\text{Zn}_2(\mu\text{-L}^2\text{-}\kappa^4\text{O,N,N,O})_2]\cdot\text{CH}_2\text{Cl}_2$ ($2\mathbf{b}\cdot\text{CH}_2\text{Cl}_2$)

The synthesis of compound $2\mathbf{b}$ was carried out as described for complex $2\mathbf{a}$ but using H_2L^2 (0.98 g, 3.0 mmol) and ZnEt_2 (3 cm^3 of a 1.0 M solution in *n*-hexane, 3.0 mmol) in thf (0.96 g, 74.4%). The crude product was recrystallized from a saturated solution in CH_2Cl_2 to give colourless crystals of $2\mathbf{b}\cdot\text{CH}_2\text{Cl}_2$ suitable for the X-ray structure determination. Anal. Calcd for $\text{C}_{41}\text{H}_{54}\text{Cl}_2\text{N}_4\text{O}_4\text{Zn}_2$: C, 56.93; H, 6.30; Cl, 8.09; N, 6.48. Found: C, 56.87; H, 6.28; Cl, 8.07; N, 6.48. ^1H NMR (500 MHz, CDCl_3 , 298 K): δ 8.07–6.59 (m, 12H, C_6H_3); 5.30 (s, 2H, CH_2Cl_2); 4.38 (d, $^2J = 11.8$ Hz, 2H, ArCH_2N); 4.20 (d, $^2J = 12.3$ Hz, 2H, ArCH_2N); 3.84 [m, 2H, $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$]; 3.05 [m, 2H, $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$]; 2.94 (d, $^2J = 11.9$ Hz, 2H, ArCH_2N); 2.88 [m, 2H, $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$]; 2.70 (d, $^2J = 12.4$ Hz, 2H, ArCH_2N); 2.60 [m, 2H, $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$]; 2.34, 2.31 [s, 6H, $\text{N}(\text{CH}_3)_2$]; 2.27, 1.97 (s, 6H, ArCH_3). ^{13}C NMR (125 MHz, CDCl_3 , 298 K): δ 165.0, 160.9, 131.6, 130.7, 125.8, 125.3, 122.9, 122.5, 121.6, 120.6, 120.1, 116.9 (C_6H_3); 60.5, 59.2 (ArCH_2N); 57.4, 50.3 ($\text{NCH}_2\text{CH}_2\text{N}$); 45.9, 47.3 [$\text{N}(\text{CH}_3)_2$]; 20.1, 20.6 (ArCH_3). ESI-MS: m/z : 781.2 [$2\mathbf{b} + \text{H}$] $^+$.

Synthesis of $[\text{Al}_2(\mu\text{-L}^1\text{-}\kappa^3\text{O,N,N,O})_2\text{Et}_2]$ (3)

Compound 3 was prepared by a similar procedure to that employed for $1\text{--}2$, but using H_2L^1 (1.04 g, 1.98 mmol),

n-hexane (30 cm^3) and AlEt_3 (2.0 cm^3 of a 1.0 M solution in *n*-hexane, 2.00 mmol). The product was precipitated as a white powder upon cooling the reaction mixture for 24 h in a refrigerator (0.94 g, 83%). Crystals suitable for X-ray structure determination were grown from a concentrated *n*-hexane solution at room temperature. Anal. Calcd for $\text{C}_{72}\text{H}_{118}\text{N}_4\text{O}_4\text{Al}_2$: C, 74.70; H, 10.27; N, 4.84. Found: C, 74.63; H, 10.25; N, 4.83. ^1H NMR (500 MHz, $\text{C}_6\text{D}_5\text{CD}_3$, 298 K): δ 7.11–6.47 (m, 12H, C_6H_3); 4.57 (d, $^2J = 13.2$ Hz, 2H, ArCH_2N); 4.42 (d, $^2J = 13.2$ Hz, 2H, ArCH_2N); 3.92 (d, $^2J = 13.8$ Hz, 2H, ArCH_2N); 3.08 (d, $^2J = 13.5$ Hz, 2H, ArCH_2N); 2.92 [br, s, 4H, $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$]; 1.98 [t, $^3J = 7.71$ Hz, 4H, $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$]; 1.77 [s, 12H, $\text{N}(\text{CH}_3)_2$]; 1.70 [br, s, 8H, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 1.53–1.38 (m, 6H, AlCH_2CH_3 overlaying with 12H, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$); 0.85, 0.77 [s, 18H, $\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 0.39, 0.15 (q, 2H, $^3J = 7.31$ Hz, AlCH_2CH_3). ^{13}C NMR (125 MHz, $\text{C}_6\text{D}_5\text{CD}_3$, 298 K): δ 159.9, 128.5, 126.2, 120.5, 116.9, 110.4 (C_6H_3); 56.2, 55.1 (ArCH_2N); 54.6 [$\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$]; 52.3 [$\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$]; 48.6 [$\text{N}(\text{CH}_3)_2$]; 44.4, 44.1 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 36.7, 36.5 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 31.4, 31.3 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 30.9, 30.7 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 30.6, 30.5 [$\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$]; 25.6 (AlCH_2CH_3); 14.3 (AlCH_2CH_3). ESI-MS: m/z : 1157.9 [$3 + \text{H}$] $^+$.

X-Ray crystallography

Crystals of H_2L^1 and the title compounds (Fig. 3–5) were mounted on low-temperature diffraction loops (100 K, Oxford Cryosystem Cooler) and measured with a KUMA KM4 four-circle diffractometer equipped a CCD area detector and a graphite monochromator utilizing Cu $\text{K}\alpha$ ($\lambda = 1.5418$ Å) for H_2L^1 and Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) for $1\mathbf{b}\cdot\text{CH}_2\text{Cl}_2$, $2\mathbf{a}\cdot\text{H}_2\text{O}$, $2\mathbf{b}\cdot\text{CH}_2\text{Cl}_2$ and 3 .¹⁷ The final cell parameters and specific data collection parameters are summarized in Table 1. The recorded data were corrected for Lorentz, polarization and absorption factors. All structures were solved by directed-methods and refined by the full-matrix least-squares program (SHELXTL).¹⁸ The carbon and oxygen bonded H-atoms were

Table 1 Summary of crystal data for compounds H_2L^1 , $1\mathbf{b}\cdot\text{CH}_2\text{Cl}_2$, $2\mathbf{a}\cdot\text{H}_2\text{O}$, $2\mathbf{b}\cdot\text{CH}_2\text{Cl}_2$ and 3

Compound	H_2L^1	$1\mathbf{b}\cdot\text{CH}_2\text{Cl}_2$	$2\mathbf{a}\cdot\text{H}_2\text{O}$	$2\mathbf{b}\cdot\text{CH}_2\text{Cl}_2$	3
Formula	$\text{C}_{34}\text{H}_{56}\text{N}_2\text{O}_2$	$\text{C}_{40}\text{H}_{52}\text{N}_4\text{O}_4\text{Mg}_2\cdot\text{CH}_2\text{Cl}_2$	$\text{C}_{68}\text{H}_{108}\text{N}_4\text{O}_4\text{Zn}_2\cdot\text{H}_2\text{O}$	$\text{C}_{40}\text{H}_{52}\text{N}_4\text{O}_4\text{Zn}_2\cdot\text{CH}_2\text{Cl}_2$	$\text{C}_{72}\text{H}_{118}\text{Al}_2\text{N}_4\text{O}_4$
Fw	524.81	786.40	1194.39	868.56	1157.66
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	$Pca2(1)$	$Pbca$	$P2_1/c$	$Pbca$	$P2_1/c$
a (Å)	12.115(3)	18.685(5)	14.542(3)	18.518(6)	21.042(6)
b (Å)	7.744(2)	19.275(5)	15.098(4)	19.252(6)	20.822(5)
c (Å)	69.22(2)	22.572(10)	31.839(5)	22.578(7)	16.111(4)
V (Å 3)	6494(3)	8129.3(5)	6970(3)	8049.2(4)	7057(3)
Z	8	8	4	8	4
D_c (Mg m $^{-3}$)	1.074	1.285	1.138	1.433	1.090
Crystal size (mm 3)	$0.28 \times 0.18 \times 0.02$	$0.21 \times 0.19 \times 0.17$	$0.12 \times 0.13 \times 0.03$	$0.06 \times 0.03 \times 0.02$	$0.21 \times 0.13 \times 0.05$
μ (mm $^{-1}$)	0.499	0.24	0.735	1.37	0.089
θ (°)	2.5–77	4–27.5	2.7–25.0	3–30.0	2–25.0
Reflections collected	30 042	55 905	77 878	64 294	82 596
Unique reflections	10 775	9240	12 324	10 668	12 520
R_{int}	0.081	0.102	0.0742	0.051	0.1640
Parameters	687	511	754	511	779
Final R_1 , wR_2 [$I > \sigma(I)$]	0.079, 0.185	0.047, 0.083	0.037, 0.0785	0.032, 0.069	0.053, 0.102
Goodness-of-fit (S)	1.066	0.997	0.941	1.000	0.896



included in calculated positions but the hydrogen atoms of hydroxyl groups in **2a**·H₂O were located from difference Fourier map and refined without any restraints. For compound **H₂L¹**, two molecules (A and B) of **H₂L¹** are present in the asymmetric unit. For the molecule (B), the C atoms of the methyl groups in the C(CH₃)₂CH₂C(CH₃)₃ substituent are disordered and were refined at 0.5 occupancy. Also in **2a**·CH₂Cl₂, some C atoms of the 'Bu moiety in the C(CH₃)₂CH₂C(CH₃)₃ substituents as well as the C atoms of the –CH₂CH₂N(CH₃)₂ sidearm in **1b**·CH₂Cl₂ and **2b**·CH₂Cl₂ are disordered and they were refined in two positions with a 0.5 (**2a**·H₂O) and 0.7 : 0.3 (**1b**·CH₂Cl₂, **2b**·CH₂Cl₂) occupancy.

CCDC reference numbers: 932554 for **H₂L¹**, 874666 for **1b**, 876629 for **2a**, 874667 for **2b**, 876628 for **3**.

Acknowledgements

The authors thank the State Committee for Scientific Research (Poland) (grant No N N204 028238) and the National Scientific Center (Poland) (grant No 2012/05/N/ST5/00697) for financial support of this work. We are grateful to Prof. Tadeusz Lis for his assistance with the X-ray crystallography of compound **H₂L¹**.

References

- For general review of the aminebis(aryloxo) metal complexes see: O. Wichmann, R. Sillanpää and A. Lehtonen, *Coord. Chem. Rev.*, 2012, **256**, 371.
- (a) F. Wolff, C. Lorber, R. Choukroun and B. Donnadieu, *Inorg. Chem.*, 2003, **27**, 7839; (b) F. Wolff, C. Lorber, R. Choukroun and B. Donnadieu, *Eur. J. Inorg. Chem.*, 2004, 2861; (c) C. Lorber, F. Wolff, R. Choukroun and L. Vendier, *Eur. J. Inorg. Chem.*, 2005, 2850; (d) A. Yeor, S. Groysman, I. Goldberg and M. Kol, *Inorg. Chem.*, 2005, **44**, 4466; (e) S. Segal, I. Goldberg and M. Kol, *Organometallics*, 2005, **24**, 200; (f) C. L. Boyd, T. Toupance, B. R. Tyrrell, B. D. Ward, C. R. Wilson, A. R. Cowley and P. Mountford, *Organometallics*, 2005, **24**, 309; (g) Y. Yao, M. Ma, X. Hu, Y. Hang, Q. Shen and W.-T. Wong, *Organometallics*, 2005, **24**, 4014; (h) Y. Sawada, K. Matsumoto, S. Kondo, H. Watanabe, T. Ozawa, K. Suzuki, B. Saito and T. Katsuki, *Angew. Chem., Int. Ed.*, 2006, **45**, 3478; (i) C. Lorber, *Pure Appl. Chem.*, 2009, **81**, 1205.
- S. Barroso, P. Adão, F. Madeira, M. Teresa Duarte, J. C. Pessoa and A. M. Martins, *Inorg. Chem.*, 2010, **49**, 7452.
- (a) M. Shavit, D. Peri, C. M. Manna, J. S. Alexander and E. Y. Tshuva, *J. Am. Chem. Soc.*, 2007, **129**, 12098; (b) C. M. Manna, M. Shavit and E. Y. Tshuva, *J. Organomet. Chem.*, 2008, **693**, 3947.
- (a) L. Rodriguez, E. Labisbal, A. Sousa-Pedrares, J. A. García-Vázquez, J. Romero, M. L. Durán, J. A. Real and A. Sousa, *Inorg. Chem.*, 2006, **45**, 7903; (b) A. Mukherjee, F. Lloret and R. Mukherjee, *Inorg. Chem.*, 2008, **47**, 4471; (c) R. K. Dean, S. L. Granville, L. N. Dawe, A. Decken, K. M. Hattenhauer and C. M. Kozak, *Dalton Trans.*, 2010, **39**, 548; (d) U. K. Das, J. Bobak, C. Fowler, S. E. Hann, C. F. Petten, L. N. Dawe, A. Decken, F. M. Kerton and C. M. Kozak, *Dalton Trans.*, 2010, **39**, 5462; (e) A. Mukherjee, F. Lloret and R. Mukherjee, *Eur. J. Inorg. Chem.*, 2010, 1032.
- (a) T. J. Boyle, H. D. Pratt, L. A. M. Ottley, T. M. Alam, S. K. McIntyre, M. A. Rodrigues, J. Farrell and C. F. Campana, *Inorg. Chem.*, 2009, **48**, 9191; (b) Q. Li, K. Nie, B. Xu, Y. Yao, Y. Hang and Q. Shen, *Polyhedron*, 2012, **31**, 58; (c) P. Kelly, M. R. Radlauer, A. J. Yanez, M. W. Day and T. Agapie, *Dalton Trans.*, 2012, **41**, 8086.
- (a) F. M. Kerton, C. M. Kozak, K. Lüttgen, C. E. Willans, R. J. Webster and A. C. Whitwood, *Inorg. Chim. Acta*, 2006, **259**, 2819; (b) C.-A. Huang and C.-T. Chen, *Dalton Trans.*, 2007, 5561; (c) W. C. Clegg, M. G. Davidson, D. V. Graham, G. Griffen, M. D. Jones, A. R. Kennedy, C. T. O'Hara, L. Russo and C. M. Thomson, *Dalton Trans.*, 2008, 1295; (d) Z. Janas, T. Nerkowski, E. Kober, L. B. Jerzykiewicz and T. Lis, *Dalton Trans.*, 2012, **41**, 442.
- Y. Sarazin, R. H. Howard, D. L. Hughes, S. M. Humphrey and M. Bochman, *Dalton Trans.*, 2006, 340.
- R. H. Howard, M. Bochman and J. A. Wright, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2006, **62**, m293.
- (a) C.-T. Chen, C.-A. Huang and B.-H. Huang, *Dalton Trans.*, 2003, 3799; (b) L. M. Alcazar-Roman, B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *Dalton Trans.*, 2003, 3082; (c) K. Phomphrai, P. Chumsaeng, P. Sangtrirutnugul, P. Kongsaree and M. Pohmakotr, *Dalton Trans.*, 2010, **39**, 1865.
- (a) Z. Tang and V. C. Gibson, *Eur. Polym. J.*, 2007, **43**, 150; (b) J. Wu, T.-L. Yu, Ch.-T. Chen and Ch.-Ch. Lin, *Coord. Chem. Rev.*, 2006, **230**, 602.
- (a) A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349; (b) M.-A. Munoz-Hernandez, T. S. Keizer, P. Wei, S. Parkin and D. A. Atwood, *Inorg. Chem.*, 2001, **40**, 6782.
- (a) J. Ejfler, K. Krauzy-Dziedzic, S. Szafert, L. B. Jerzykiewicz and P. Sobota, *Eur. J. Inorg. Chem.*, 2010, 3602; (b) R. H. Howard, C. Alonso-Moreno, L. M. Broomfield, D. L. Hughes, J. A. Wright and M. Bochmann, *Dalton Trans.*, 2009, 8667; (c) Y. Xiao, Z. Wang and K. Ding, *Macromolecules*, 2006, **39**, 128; (d) L. E. Breyfogle, C. K. Williams, V. G. Young Jr., M. A. Hillmyer and W. B. Tolman, *Dalton Trans.*, 2006, 928.
- S. Groysman, E. Sergeeva, I. Goldberg and M. Kol, *Eur. J. Inorg. Chem.*, 2006, 2739.
- (a) I. Taden, H.-C. Kang, W. Massa, T. S. Spaniol and J. Okuda, *Eur. J. Inorg. Chem.*, 2000, 441; (b) Y.-C. Liu, B.-T. Ko and C.-C. Lin, *Macromolecules*, 2001, **34**, 6196; (c) P. Hormnirum, E. L. Marshall, V. C. Gibson, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2004, **126**, 2688; (d) J. Lewiński, J. Zachara and I. Justyniak, *Organometallics*, 1997, **16**, 4597; (e) J. A. Francis, S. G. Bott and A. R. Baron, *J. Chem. Soc., Dalton Trans.*, 1998, 3305; (f) Z. Janas,



- L. B. Jerzykiewicz, P. Sobota and K. Szczegot, *Organometallics*, 2005, **24**, 3987; (g) A. L. Johnson, M. G. Davidson, Y. Pérez, M. D. Jones, N. Merle, P. R. Raithby and S. P. Richards, *Dalton Trans.*, 2007, 5551; (h) N. Tiempos-Flores, A.-J. Matta-Magaña, V. Montiel-Palma, S.-A. Costès-Llamas and M.-A. Muñoz-Hernández, *Dalton Trans.*, 2010, **39**, 4312.
- 16 C. P. Radano, G. L. Baker and M. R. Smith, *J. Am. Chem. Soc.*, 2000, **122**, 1552.
- 17 Oxford Diffraction, *CrysAlis CCD and CrysAlis RED*. Oxford Diffraction Poland, Wroclaw, Poland, 2009.
- 18 Bruker, *SHELXTL. Version 6.14*. Bruker AXS Inc., Madison, Wisconsin, USA, 2003.

