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# *N*-Bridged bis-amidine *N*-oxides – a versatile platform in metallosupramolecular chemistry

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**An *N*-bridged bis-amidine *N*-oxide (AMOX) ligand was synthesized, characterized, and used as a synthon for AMOX-based supramolecular architectures. Different multimetallic compounds were obtained upon its coordination with transition metal ions: a dinuclear discrete assembly with Ni(II) and a luminescent Zn(II) 1D-metallopolymer, as confirmed by their solid-state structures.**

Due to their unique properties, coordination compounds are suitable and attractive for a wide range of applications in well-established and emergent domains, as well as for fundamental research.[1] Therefore, they are successfully used in fields ranging from catalysis and solar energy conversion/storage to materials and life sciences.[1] More specifically, metal ion-based coordination compounds in discrete,[2] oligo- or polymeric[3] metallosupramolecular assemblies have been used as synthons for creating functional materials and devices.[2b,3c,d,4] The successful use of luminescent polymetallic species[5] (based on Earth-abundant and biocompatible ions such as Zn(II))[6] in optoelectronic devices (*e.g.*, OLEDs)[6b,7] perfectly highlights this point. Thus, the study of coordination compounds is equally important from fundamental and applied research perspectives for advancing the field of functional materials and for developing new technologies. Moreover, the appeal of multimetallic systems arises from their improved properties *vs.* those of monometallic ones.[8]

Based on the success of 8-hydroxyquinoline-type ligands,[9] amidine-*N*-oxides (AMOXs, also called α-aminonitrones and *N*-hydroxyamidines) have piqued our interest in investigating their applications in coordination chemistry.[6b,10] AMOXs are anionic bidentate N,O-ligands that act as good chelators for metal ions and present electronic delocalization in the amidine backbone. Furthermore, they offer the possibility to modulate their chelation capacity by fine-tuning their electronic and steric properties by varying the substitution pattern on the three atoms of the amidine moiety.[11,12]

In this work, we present the preliminary results obtained using bis-AMOX ligands in metallosupramolecular chemistry. Thus, *N*-bridged bis-AMOXs were synthesized in order to be tested as synthons for AMOX-based supramolecular architectures dictated by the coordination vectors of the ligand (*e.g.*, parallel, antiparallel, at fixed angles) and the geometry of the metal ions (Fig. S1, SI).[3b,13] Discrete structures such as

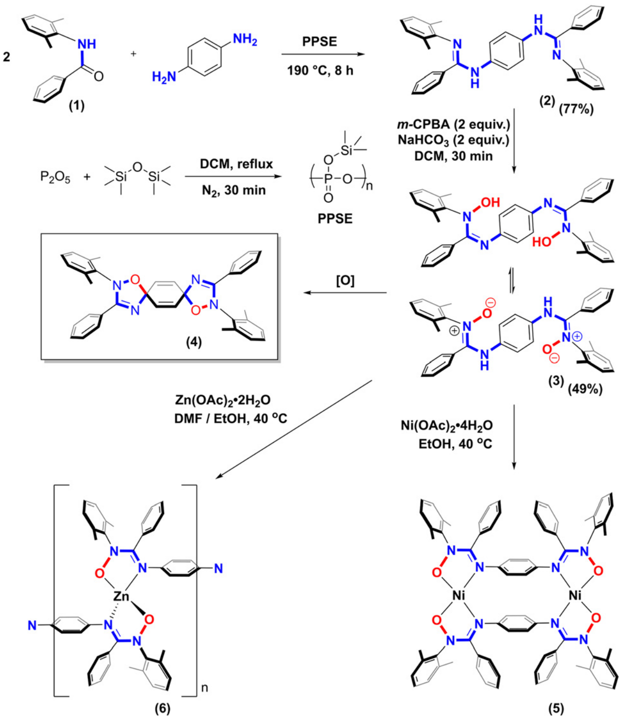

**Fig. 1** Synthesis of compounds **2–6**: *N*-bridged bis-amidine precursor (**2**), *N*-bridged bis-AMOX ligand (**3**), oxidized bis-AMOX (**4**), Ni(II) coordination dimer (**5**), and Zn(II) coordination polymer (**6**).

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2 : 2 metallacycles or grids are expected upon coordination of the *N*-bridged bis-AMOX ligand proposed herein with tetrahedral metal ions (*e.g.*, Zn(II)) (Fig. S2).

The synthesis of the compounds presented in this work is shown in Fig. 1 and detailed in the SI. The parent **bis-amidine** (**2**) is prepared in good yield (77%) by condensation between two equivalents of the **amide** (**1**) (previously reported)[14] and 1,4-phenylenediamine, in polyphosphoric acid trimethylsilyl ester (PPSE), followed by basic treatment.[15] The PPSE-promoted synthesis for affording the *N*-bridged bis-amidine compound was optimized under the conditions presented above (8 h at 190 °C); at shorter reaction times, unreacted amide is present, and at longer reaction times, secondary products are formed. *N*-Oxidation of the parent *N*-bridged **bis-amidine** (**2**) with two equivalents of *meta*-chloro-peroxybenzoic acid (*m*-CPBA) in dichloromethane (DCM) (10–15 mM) at room temperature affords the *N*-bridged **bis-AMOX** ligand (**3**) in reasonable yield (49%) after purification by flash chromatography on silica.[16] Major secondary products identified in the reaction are the AMOX-amidine† and the **oxidized bis-AMOX** (**4**). It was found that at higher concentrations of reactants, the formation of **4** is favored. As expected, **4** is also obtained as the major product when an excess of *m*-CPBA is used. Different multimetallic architectures were obtained upon coordination of the *N*-bridged **bis-AMOX** ligand **3** with metal ions: a discrete self-assembly of a 2 : 2 metallacycle with Ni(II) (**5**) and a 1D-metallopolymer with Zn(II) (**6**) (Fig. 1).

Compounds **2–5** were characterized by IR and NMR spectroscopy techniques, mass spectrometry (MS) and elemental analysis (EA) (details are given in the SI). IR spectra (Fig. S9–13) reveal the presence of expected bands characteristic of N–H secondary amine (3300–3500 cm$^{-1}$) bond vibration in **2** and C–H saturated and unsaturated (2800–3100 cm$^{-1}$), C═N imine and C═C aromatic (1590–1690 cm$^{-1}$), as well as C–N (1400–1450 cm$^{-1}$) bond vibrations in **2–5**. The corresponding N–O band appears at 937 cm$^{-1}$ in **3** and shifts to higher frequencies upon complexation (966 cm$^{-1}$ in **5** and 961 cm$^{-1}$ in **6**), as previously observed for other AMOX-based coordination compounds.[12c] $^{1}$H, COSY, and $^{13}$C NMR spectra for **2–5** are presented in Fig. S14–S26, with full assignment of proton resonances. Of note, the $^{1}$H NMR analysis of **bis-amidine** (**2**) was hindered by the solvent-dependent fluxionality of the amidine moieties in solution. The best results were obtained in DMSO-$d^{6}$ at a high temperature (110 °C) (Fig. S14–S17). Furthermore, the Ph-bridge proton resonances are observed at a chemical shift of 6.48 ppm in **3** and are shifted upfield in **4** and **5** due to the shielding effect induced by heterocycle formation and complexation, respectively. For **6**, its very poor solubility hindered its characterization in solution.

The solid-state structures of **3**, **4**, **5**, and **6** were also obtained (Fig. 2, Fig. 3, and Fig. S27–S30). Crystal data, data collection, and structure refinement details are summarized in Table S1. For **3**, the amidine oxide form was found in the solid state. The N–***H*** atoms were located from a difference Fourier map. The presence of cyclic dimers *via* N–H⋯O ($d$ = 1.90(3) Å) hydrogen bonds was also observed in the crystal packing of **3** (Fig. S27). The solid-state structure of **4** highlights the oxidized form of **bis-AMOX** (**3**) with the formation of five-membered C$^{\mathrm{Ph}}$NCNO heterocycles orthogonal (88(1)°) to the phenyl bridge (Fig. 1 and Fig. S28). Achieving this type of structure underlines the great potential of *N*-bridged AMOX ligands as precursors for heterocyclic compounds in organic chemistry.[17]

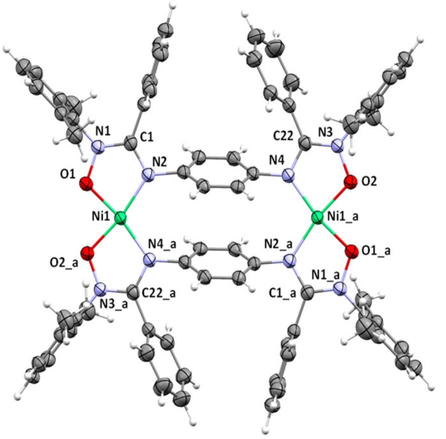

**Fig. 2** The solid-state structure of **5**. ORTEP view with ellipsoids at the 50% probability level (symmetry code: 1 – *x*, 1 – *y*, 1 – *z*). Co-crystallized ethanol molecules are omitted for clarity. Ni⋯Ni distance, 7.92(1) Å.

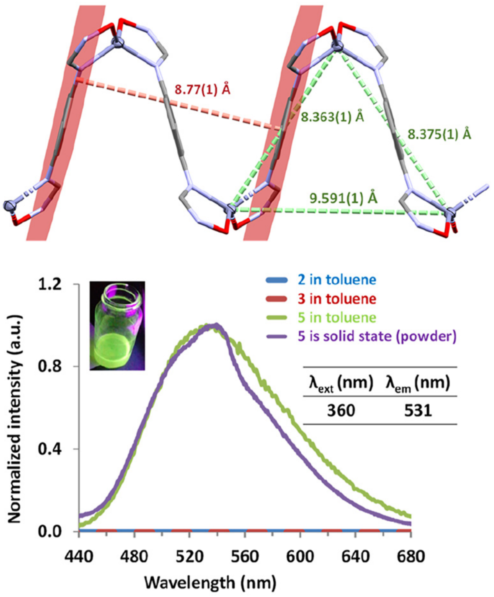

**Fig. 3** The solid-state structure of **6** (top). Phenyl and 2,6-dimethylphenyl substituents as well as hydrogen atoms and co-crystallized toluene molecules were omitted for clarity. Emission spectra (bottom): **Zn(II) metallopolymer** (**6**) in toluene (green) and in the solid state (powder) (purple); the *N*-bridged **bis-AMOX** ligand (**3**) in toluene (red) and the *N*-bridged **bis-amidine** precursor (**2**) in toluene (blue).

The solid-state structure of **5** (Fig. 2 and Fig. S29) confirms the formation of the *N*-bridged AMOX coordination Ni(II) dimer.[18] As expected on electronic grounds for a Ni(II) $d^{8}$ metal ion in a four-coordinate medium ligand field environment, a square-planar geometry is found around the metal ion centers.[18,19] The geometrical constraints of the bis-AMOX ligand impose, though, a slight distortion ($\tau_4$ = 0.17)[20] from the ideal square-planar geometry. Strong bridge$^{Ph}$ to bridge$^{Ph}$ π–π interactions (interplanar distance 2.98(1) Å) also exist in **5**, and the Ni⋯Ni distance (7.92(1) Å) is shorter than those found in phenyl-bridged Ni dimers of Schiff base ligands (8.12(1) Å).[21] Noteworthily, the solid-state structure of the Ni dimer demonstrates the potential of similar *N*-bridged bis-AMOX-based compounds with paramagnetic metal ions to exhibit interesting magnetic properties.[10a,b,22]

The complexation of the *N*-bridged **bis-AMOX** ligand (**3**) (presenting the possibility to have parallel coordination vectors) with Zn(II) metal-ions (with preference for tetrahedral geometry) was realized in an attempt to synthesize a grid-type compound (Fig. S2). However, a 1D-metallopolymer was obtained, as shown by the solid-state structure of **6** (Fig. 3 and Fig. S30). The compound is an air-stable yellow solid, highly insoluble in most common solvents. Poor quality X-ray crystals (very thin yellow needles) were obtained from hot toluene by slow evaporation. The solid-state structure highlights a 1D coordination polymer, with the shortest Zn⋯Zn distance of 8.363(1) Å (Fig. 3, top). The Zn(II) metal-ions display a pseudotetrahedral geometry ($\tau_4$ = 0.74),[20] as expected on steric grounds for a $d^{10}$ ion in a 4-coordinate bidentate environment.[23]

The electronic spectra for **6** ($\lambda_{\text{max abs}}$ = 360 nm), together with those for the **bis-AMOX** ligand (**3**) and the corresponding parent **bis-amidine** (**2**) (in toluene), are shown in Fig. S31. They display characteristic π–π* ligand-centered transitions.

Furthermore, the Zn(II) metallopolymer is luminescent ($\lambda_{\text{max em}}$ = 531 nm) (Fig. 3), in line with what was also found for other Zn(II) monomers, dimers, trimers and coordination polymers.[24] Moreover, **6** has good thermal stability, as shown by its TGA profile with a decomposition temperature ($T_d$) (measured at 5% weight loss) of 320 °C (Fig. S32). These properties endow **6** with potential for use in optoelectronic devices (*e.g.*, OLEDs).[6b] Its solubility problem could be solved by introducing solubilizing groups on the AMOX ligands. Fine-tuning of the band gap for these types of compounds can be achieved by modifying the substitution pattern of the ligand.[10c]

In summary, an *N*-bridged bis-AMOX ligand was synthesized and used as a synthon for AMOX-based supramolecular architectures. Different multimetallic compounds were obtained upon coordination of the ligand with transition metal ions: a dinuclear discrete assembly with Ni(II) and an emissive 1D-metallopolymer with Zn(II) ions, as confirmed by their solid-state structures. Upon oxidation of the AMOX ligand, an interesting heterocyclic compound was also formed. Thus, the results herein demonstrate the potential of *N*-bridged bis-AMOX ligands as synthons for metallosupramolecular architectures and as precursors for heterocyclic compounds. For future perspectives, the Ni-dimer will be evaluated for catalytic activity, and the analog Cu(II) dimer will be synthesized and investigated for its catalytic and magnetic properties. The Zn(II) grid species is still to be obtained; screening of different conditions (solvent/temperature/stoichiometry) is being pursued. Examining H-bonding in bis-AMOX ligands and exploiting the cooperative effects of coordination and H-bonding in AMOX-amidine† type compounds are also of interest from a crystal engineering point-of-view. Extending ligand design to multifunctional AMOXs by structural variation (*e.g.*, introducing pendant pyridine(s), phosphine(s), to the AMOX backbone) and coordination to different metal ions could lead to interesting metallosupramolecular architectures and promising candidates for active components in functional materials. Selective binding of metal ions by specific ligand design is also being targeted. This work is currently underway in our laboratories.

## Author contributions

Mathieu Lepage: formal analysis, investigation (synthesis and characterization), validation, and writing – review & editing. Marine Devos: investigation (synthesis and characterization). Sammy Touaibia: investigation (synthesis and characterization). Garry S. Hanan: funding acquisition, project administration, resources, supervision, and writing – review & editing. Mihaela Cibian: conceptualization, formal analysis, funding acquisition, investigation (synthesis and characterization, X-ray diffraction, absorption and emission measurements, and DFT calculations), project administration, resources, validation, supervision, writing – original draft, and writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included in the main article (Fig. 1–3) and as part of the supplementary information (SI). Supplementary information is available: material and instrumentation; detailed experimental procedure; IR spectra, NMR spectra, X-ray diffraction measurements and the solid state structure determination; electronic spectra; thermogravimetric analysis; atomic coordinates tables for DFT optimized structures. See DOI: https://doi.org/10.1039/d6dt01182a.

CCDC 2322646, 2322647, 2322741 and 2322755 for compounds **3**, **4**, **5**, and **6** contain the supplementary crystallographic data for this paper.[25a–d]

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† The AMOX-amidine denomination is used for the mono-oxidized bis-amidine, the *N*-bridged compound bearing an AMOX moiety and an amidine one; this compound was obtained as a secondary product in the *N*-oxidation reaction.

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