



Synthesis and structural characterization of lithium, sodium and potassium complexes supported by a tridentate amino-bisphenolate ligand

Clara J. Durango-García^a, Ernesto Rufino-Felipe^b, Marcela López-Cardoso^b, Miguel-Ángel Muñoz-Hernández^b, Virginia Montiel-Palma^{b,*}

^a Facultad de Ciencias, Universidad Antonio Nariño sede Armenia, Av. Bolívar 49 Norte - 30, Armenia-Quindío, Colombia

^b Centro de Investigaciones Químicas, Instituto de Investigación en Ciencias Básicas y Aplicadas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Col. Chamilpa, Cuernavaca, Morelos 62209 Mexico

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ABSTRACT

Reactions of methylamino-*N,N*-bis(2-methylene-4,6-di-*tert*-butylphenol) (**1**) with one or two equivalents of bulk Li, Na or K metals in THF or DMSO render mono or dialkali metal complexes depending on the stoichiometric ratio of the reactants. The metal-methylamino-*N*-(2-methylene-4,6-*tert*-butylphenol)-*N*-(2-methylene-4,6-*tert*-butylphenolate) complexes, **2Li**, **2Na** and **2K**, are generated upon the substitution of a single phenol hydrogen of **1**. In the solid state, complex **2Na** is a dimer due to the establishment of two symmetric hydrogen bonds between two adjacent molecules. The Na center also engages into the formation of a ten-membered metallacycle ring with a butterfly-like structure. Due to dimerization, an intermolecular six-membered core is formed involving two sodium and four oxygen atoms. The weakly coordinated nitrogen atom from the ligand is nearly perpendicular to the hexagonal core. The dimetal-methylamino-*N,N'*-bis(2-methylene-4,6-di-*tert*-butylphenolate) complexes, **3Li**, **3Na** and **3K** result from metal substitution of the two phenol hydrogens from ligand **1**. The SC-XRD structures of **3Li** and **3Na** are discreet, each incorporating two metal atoms in different coordination environments. Ten-membered rings with boat-boat conformations are also observed as are rhombic central M₂O₂ cores. The molecular structure of **3K** in DMSO shows a higher degree of aggregation. It effectively comprises four K atoms, two ligand backbones and seven solvent molecules forming a central four-membered K₂O₂ ring perpendicular to an eight-membered structure formed also by K and O atoms spanning over the two ligand moieties.

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1. Introduction

The coordination chemistry of a number of ligands has flourished partly owing to the increasing interest for the development of efficient catalytic systems for a variety of chemical reactions [1]. Understanding the fundamental aspects of the coordination and structure of the chemical systems can have a profound impact if one aims at designing more efficient and environmentally friendly catalysts. As an illustration, Ma and coworkers reported on a family of potassium amino-phenolate complexes capable of polymerizing *rac*-lactide with high monomer conversions yet poor selectivity and

attributed this behavior to the coordination modes of K as well as steric effects [2]. Indeed, in recent years alkali metal complexes have been pointed out as successful, innocuous alternatives to the more expensive transition metals for a variety of applications [3–5]. Due to their ability to coordinate a wide range of metals, ligands based on N- and O-donor atoms, amongst which Schiff bases and aminophenolates are preferred options, have been employed as alternatives to non-metallocene olefin and ester polymerization systems, including biodegradable polymers [4,6–9]. With regards to aminophenolates, studies including systematic comparisons between group 1 metals, remain rare [10,11]. In those studies however, it has been noticed that even small changes in the ligand and solvent result in important differences in the structure and chemical reactivity of the complexes [12].

In light of this, we now wish to report on the reactivity of the

* Corresponding author.

E-mail address: vmontielp@uaem.mx (V. Montiel-Palma).

tridentate proligand methylamino-*N,N*-bis(2-methylene-4,6-*tert*-butylphenol) (**1**) towards bulk alkali metals Li, Na or K. We show reactions take place resulting in formal substitution of one or two of the phenol hydrogens by a metal cation with concomitant dihydrogen gas release.

2. Materials and methods

2.1. General details

All manipulations were carried out under an atmosphere of argon using standard Schlenk line techniques or an MBraun glovebox under argon, unless otherwise indicated. All commercial reagents were purchased from Aldrich or Merck and used as received. Solvents were distilled under nitrogen from the appropriate drying agent. CDCl_3 and DMSO-d_6 were stored under molecular sieves. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^7Li NMR spectra were recorded either on a Varian Mercury 200 MHz or a Varian Unity 400 MHz spectrometers at room temperature. Elemental analyses were performed using Elementar Vario EL-III equipment. Infrared spectra were prepared as KBr pellets under argon in a glovebox and were recorded on a Nicolet 6700 spectrometer.

2.2. Single crystal X-ray diffraction (SC-XRD)

SC-XRD data for **2Na**, **3Li** and **3Na** were collected using the program SMART [13] on a Bruker APEX CCD diffractometer with monochromatized $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell refinement and data reduction were carried out with the use of the program SAINT, the program SADABS was employed to make incident beam, decay and absorption corrections in the SAINT-Plus v. 6.0 suite [14]. Then, the structures were solved by direct methods with the program SHELXS and refined by full-matrix least-squares techniques with SHELXL in the SHELXTL v. 6.1 suite [15]. X-ray intensity data for **3K** was collected using the program *CrysAlisPro* on a four-circle SuperNova, Dual EosS2 CCD diffractometer with monochromatic $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). Cell refinement, data reduction, incident beam, decay and absorption corrections were carried out with the use of the program *CrysAlisPro*. Using *Olex 2*, the structure was solved by direct methods with the program SHELXT and refined by full-matrix least-squares techniques with SHELXL. Hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. The final models involved anisotropic displacement parameters for all non-hydrogen atoms. The crystal structure data was deposited at the Cambridge Crystallographic Data Center and further details of the structure analysis are given in the ESI.

2.3. Synthesis of proligand methylamino-*N,N*-bis(2-methylene-4,6-*di-tert*-butylphenol), **1**

Methylamino-*N,N*-bis(2-methylene-4,6-*di-tert*-butylphenol) (**1**) was synthesized according to reported procedures [16,17] by Mannich condensation of methylamine, paraformaldehyde and 2,4-*di-tert*-butylphenol.

2.4. Synthesis of sodium-methylamino-*N*-(2-methylene-4,6-*tert*-butylphenol)-*N*'-(2-methylene-4,6-*tert*-butylphenolate), **2Na**

Equimolar amounts of Na (0.43 mmol, 10 mg) and **1** (0.43 mmol, 200 mg) were refluxed for 48 h. After this time, the reaction mixture was filtered off via cannula to remove the unreacted solids. The solution was then dried under vacuum to yield a fine white solid. Crystals suitable for SC-XRD were grown from concentrated THF solutions at 257 K. **2Na** was obtained as a THF adduct. Yield

66%. ^1H NMR (CDCl_3 , 400 MHz, 298 K), δ (ppm): 1.32 (s, 18H, CH_3), 1.42 (s, 18 H, CH_3), 2.60 (s, 3H, NCH_3), 3.96 (br s, 2H, CH_2), 4.76 (br s, 2H, CH_2), 6.81 (d, $^4J_{\text{HH}}$ 2.2 Hz, 2H, $\text{CH}_{\text{aromatic}}$), 7.18 (d, $^4J_{\text{HH}}$ 2.2 Hz, 2H, $\text{CH}_{\text{aromatic}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.61 MHz, 298 K), δ (ppm): 30.0 (CH_3), 31.7 (CH_3), 46.8 (NCH_3), 55.8 (CH_2), 126.5 ($\text{C}_{\text{aromatic}}$), 127.3 ($\text{C}_{\text{aromatic}}$), 128.4 ($\text{C}_{\text{aromatic}}$), 129.2 ($\text{C}_{\text{aromatic}}$), 141.0 ($\text{C}_{\text{aromatic}}$). Anal. Calcd for $\text{C}_{39}\text{H}_{64}\text{NNaO}_4$: C, 73.89; H, 10.18; N, 2.21. Found: C, 74.08; H, 10.44; N, 2.28.

2.5. Synthesis of lithium-methylamino-*N*-(2-methylene-4,6-*tert*-butylphenol)-*N*'-(2-methylene-4,6-*tert*-butylphenolate), **2Li**

To a Schlenk flask containing a solution of **1** (360 mg, 0.8 mmol) in 15 mL of THF, 0.8 mmol (6 mg) of finely cut Li were added. The mixture was refluxed for 48 h under vigorous stirring. After this time, the reaction mixture was filtered off via cannula to remove the residual solid. The solution was then dried under vacuum and the remaining fine white solid crystallized from THF. The white crystals were not suitable for a SC-XRD experiment. **2Li** was obtained as a THF adduct. Yield 68%. ^1H NMR (CDCl_3 , 400 MHz, 298 K), δ : 1.13 (s, 18H, CH_3), 1.34 (s, 18H, CH_3), 1.84 (s, 3H, NCH_3), 2.88 (br, $\omega_{1/2}$ 34 Hz, 2H, CH_2), 4.17 (br, $\omega_{1/2}$ 46 Hz, 2H, CH_2), 6.71 (br, 2H, $\text{CH}_{\text{aromatic}}$), 7.04 (br, 2H, $\text{CH}_{\text{aromatic}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.61 MHz, 298 K), δ : 140.89 ($\text{C}_{\text{aromatic}}$), 137.32 ($\text{C}_{\text{aromatic}}$), 133.07 ($\text{C}_{\text{aromatic}}$), 125.17 ($\text{C}_{\text{aromatic}}$), 123.24 ($\text{C}_{\text{aromatic}}$), 121.98 ($\text{C}_{\text{aromatic}}$), 63.56 (CH_2), 39.55 (NCH_3), 35.35 ($\text{C}-\text{CH}_3$), 34.04 ($\text{C}-\text{CH}_3$), 32.08 (CH_3), 29.84 (CH_3). ^7Li NMR (CDCl_3 , 155.45 MHz, 298 K) δ : -1.81 (br s). Anal. Calcd. for $\text{C}_{39}\text{H}_{64}\text{LiNO}_4$: C, 75.81; H, 10.44; N, 2.27. Found: C, 76.25; H, 9.99; N, 2.38.

2.6. Synthesis of potassium-methylamino-*N*-(2-methylene-4,6-*tert*-butylphenol)-*N*'-(2-methylene-4,6-*tert*-butylphenolate), **2K**

To a solution of **1** (200 mg, 0.43 mmol) in 8 mL THF, 17 mg (0.43 mmol) of finely cut K were added. The reaction mixture was refluxed for 3 h after which time all the metal had been consumed. The solution was dried under vacuum, washed three times with 0.5 mL of cold hexane and recrystallized from concentrated THF rendering a pale yellow solid. **2K** was obtained as a THF adduct. Yield 71%. ^1H NMR (CDCl_3 , 400 MHz, 298 K), δ (ppm): 1.25 (s, 18H, CH_3), 1.35 (s, 18 H, CH_3), 2.56 (s, 3H, NCH_3), 3.93 (s, 2H, CH_2), 4.74 (s, 2H, CH_2), 6.77 (d, $^4J_{\text{HH}}$ 2.8 Hz, 1H, $\text{CH}_{\text{aromatic}}$), 7.13 (d, $^4J_{\text{HH}}$ 2.8 Hz, 1H, $\text{CH}_{\text{aromatic}}$), 7.20 (d, $^4J_{\text{HH}}$ 2.8 Hz, 1H, $\text{CH}_{\text{aromatic}}$), 7.26 (d, $^4J_{\text{HH}}$ 2.8 Hz, 1H, $\text{CH}_{\text{aromatic}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.61 MHz), δ (ppm): 150.3 ($\text{C}_{\text{aromatic}}$), 148.2 ($\text{C}_{\text{aromatic}}$), 142.2 ($\text{C}_{\text{aromatic}}$), 136.6 ($\text{C}_{\text{aromatic}}$), 125.1 ($\text{C}_{\text{aromatic}}$), 123.7 ($\text{C}_{\text{aromatic}}$), 123.2 ($\text{C}_{\text{aromatic}}$), 122.1 ($\text{C}_{\text{aromatic}}$), 122.0 ($\text{C}_{\text{aromatic}}$), 118.9 ($\text{C}_{\text{aromatic}}$), 116.0 ($\text{C}_{\text{aromatic}}$), 53.2 (CH_2), 40.1 (NCH_3), 35.2 ($\text{C}-\text{CH}_3$), 34.5 ($\text{C}-\text{CH}_3$), 31.9 (CH_3), 29.9 (CH_3). Anal. Calcd for $\text{C}_{39}\text{H}_{64}\text{KNO}_4$: C, 72.06; H, 9.92; N, 2.15. Found: C, 72.11; H, 9.86; N, 2.16.

2.7. Synthesis of dilithium-methylamino-*N,N'*-bis(2-methylene-4,6-*di-tert*-butylphenolate), **3Li**

200 mg (0.43 mmol) of **1** and 6 mg (0.9 mmol) of oil-free Li were refluxed in THF for 48 h. Yellow crystals suitable for X-ray analysis were grown from concentrated THF-hexane solutions at 273 K. Yield 75%. **3Li** was also obtained as a THF adduct. ^1H NMR (CDCl_3 , 400 MHz), δ (ppm): 1.18 (s, 18H, CH_3), 1.42 (s, 18H, CH_3), 1.95 (s, 3H, NCH_3), 2.73 (d, $^2J_{\text{HH}}$ 11.6 Hz, 2H, CH_2), 4.11 (d, $^2J_{\text{HH}}$ 11.6 Hz, 2H, CH_2), 6.80 (d, $^4J_{\text{HH}}$ 2.2 Hz, 2H, $\text{CH}_{\text{aromatic}}$), 7.10 (d, $^4J_{\text{HH}}$ 2.2 Hz, 2H, $\text{CH}_{\text{aromatic}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.61 MHz), δ (ppm): 166.2 ($\text{C}_{\text{aromatic}}$), 136.9 ($\text{C}_{\text{aromatic}}$), 132.3 ($\text{C}_{\text{aromatic}}$), 127.3 ($\text{C}_{\text{aromatic}}$), 125.6 ($\text{C}_{\text{aromatic}}$), 123.0 ($\text{C}_{\text{aromatic}}$), 65.1 (CH_2), 40.4 (NCH_3), 36.1 ($\text{C}-\text{CH}_3$), 34.5 ($\text{C}-\text{CH}_3$), 32.7 (CH_3), 30.5 (CH_3). ^7Li NMR (THF- d_8 , 155.45 MHz,

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