Polyhedron 94 (2015) 59–66

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Copper(I) and silver(I) complexes containing the enantiopure *N*,*N*-bidentate 1,3-bis[4′-(*S*)-isopropyloxazolin-2′-yl]benzene ((*S*,*S*)-^{i}Pr-pheboxH) ligand

Esmeralda Vega, Eire de Julián, Gustavo Borrajo, Josefina Díez, Elena Lastra, M. Pilar Gamasa *

Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica “Enrique Moles” (Unidad Asociada al CSIC), Universidad de Oviedo, 33006 Oviedo, Spain

A R T I C L E I N F O

Article history:
Received 5 February 2015
Accepted 11 April 2015
Available online 18 April 2015

Keywords:
Copper(I) complexes
Silver(I) complexes
Enantiopure complexes
1,3-Bis[4′-(*S*)-isopropyloxazolin-2′-yl]benzene ligand
Bis(oxazoline) ligand

A B S T R A C T

The reaction of CuX (X = I, Br, Cl) with (*S*,*S*)-^{i}Pr-pheboxH = 1,3-bis[4′-(*S*)-isopropyloxazolin-2′-yl]benzene in 2:1 molar ratio allows us to synthesize tetranuclear complexes $[Cu_4X_4(\kappa^2\text{-}N,N\text{-}^i\text{Pr-pheboxH})_2]$ (X = Cl (**1**), Br (**2**), I (**3**)). The polymeric species $[Cu_4I_4(\kappa^2\text{-}N,N\text{-}^i\text{Pr-pheboxH})_2]_n$ (**4**) has been prepared by reaction of CuI with (*S*,*S*)-^{i}Pr-pheboxH in 1.5:1 molar ratio. Also, polymeric silver species $\{[Ag(\kappa^2\text{-}N,N\text{-}^i\text{Pr-pheboxH})][X]\}_n$ (X = CF_3SO_3 (**7a**), SbF_6 (**7b**), PF_6 (**7c**)) have been synthesized by reaction of the corresponding silver salt and (*S*,*S*)-^{i}Pr-pheboxH in 1:1 molar ratio. The structures of the tetranuclear complexes **1**–**3** as well as of the polymeric species $[Cu_4I_4(\kappa^2\text{-}N,N\text{-}^i\text{Pr-pheboxH})_2]_n$ (**4**) and $\{[Ag(\kappa^2\text{-}N,N\text{-}^i\text{Pr-pheboxH})][PF_6]\}_n$ (**7c**) have been determined by single crystal X-ray analysis.

1. Introduction

Over the last two decades, enantiopure bis(oxazoline) derivatives have been recognized as one of the most useful type of ligands in metal-catalyzed asymmetric transformations. This fact is not only a consequence of their high induction efficiency but also on their ability to coordinate to a large number of metals [1,2]. Despite that bis(oxazoline) ligands wherein the two oxazoline rings are connected by a one-carbon spacer are most commonly employed, other systems containing spacer units with varied nature, size, and flexibility have also been reported [1c,f,g]. Moreover, metal complexes containing monoanionic bisoxazolinate ligands have been successfully employed in asymmetric catalysis in the last years [3].

On the other hand, the *N*,*C*,*N*-tridentate anionic ligands 2,6-bis[4′-R-oxazolin-2′-yl)]phenyl (R-phebox, R = ^{i}Pr, Ph, ^{t}Bu, Me, Bn) represent a related type of C_2-symmetric chiral ligands that have been successfully employed in asymmetric catalysis in the last years [4]. However, as far as we are aware, *N*,*N*-bidentate complexes containing the enantiopure 1,3-bis[4′-R-oxazolin-2′-yl]benzene (R-pheboxH) ligand have not been reported as yet [5]. Therefore, we herein report on the synthesis of copper(I) and silver(I) complexes containing the enantiopure (*S*,*S*)-^{i}Pr-pheboxH ligand. This study has permitted to access a variety of metal complexes with great structural diversity. The crystal structures of complexes **1**, **2**, **3**, **4** and **7c** have been determined by single-crystal X-ray diffraction analysis. In accordance with the presence of an enantiopure ligand, complexes **1**–**4** and **7c** crystallize in chiral space groups. The absolute structures have been confirmed by refinement of the Flack parameter.

2. Experimental

2.1. General procedures

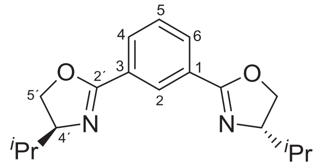
The reactions were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. (*S*,*S*)-^{i}Pr-pheboxH was prepared by reported method [6]. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature, in ca. 3×10^{-4} mol L^{-1} acetone or nitromethane solutions, with a Jenway PCM3 crison EC-meter Basic 30+ conductimeter. The C, H and N analyses were carried out with a LECO CHNS-TruSpec and a Perkin–Elmer 240-B microanalyzers (inconsistent analyses were found for complex **4**). Mass spectra (FAB) were recorded using a VG-AUTOSPEC spectrometer, operating in the positive mode, and using 3-nitrobenzyl alcohol (NBA) as the matrix (complexes **5**, **6**, **7a** and **7b**). NMR spectra were

---

* Corresponding author. Fax: +34 985103446.
E-mail address: pgb@uniovi.es (M.P. Gamasa).

http://dx.doi.org/10.1016/j.poly.2015.04.014
0277-5387/

obtained on Bruker spectrometers (AV 400 operating at 400.13 (^{1}H) and 100.61 MHz (^{13}C) or DPX300 operating at 300.13 (^{1}H) and 75.48 (^{13}C) MHz). DEPT experiments were carried out for all the compounds. Chemical shifts are reported in parts per million and referenced to TMS as standard. Coupling constants *J* are given in hertz. The following atom labels have been used for the ^{1}H and ^{13}C{^{1}H} spectroscopic data of the (*S*,*S*)-^{i}Pr-pheboxH.



2.2. Synthesis and characterization of complexes [Cu$_4$X$_4$(κ^2-N,N-^{i}Pr-pheboxH)$_2$] (X = Cl (**1**), Br (**2**), I (**3**))

To a solution of (*S*,*S*)-^{i}Pr-pheboxH (0.051 g, 0.173 mmol) in dichloromethane (15 mL), the corresponding copper(I) salt CuX (X = Cl, Br, I) (0.347 mmol) was added and the mixture stirred at room temperature during 24 h. Then, the reaction mixture was filtered via cannula, concentrated under reduced pressure to *ca.* 2 mL and diethyl ether/*n*-hexane (1:2) (30 mL) was added. The resulting solid was washed with *n*-hexane (3 × 5 mL) and vacuum-dried.

2.2.1. [Cu$_4$Cl$_4$(κ^2-N,N-^{i}Pr-pheboxH)$_2$] (**1**)

Yield: 90% (0.161 g). Color: yellow. *Anal.* Calc. for $C_{36}H_{48}N_4O_4Cu_4Cl_4 \cdot 0.5CH_2Cl_2$: C, 42.18; H, 4.75; N, 5.39. Found: C, 42.20; H, 4.66; N, 5.39. Molar conductivity (nitromethane, 293 K, S·cm^2·mol^{-1}): 9.1. ^{1}H NMR (300.13 MHz, CD_2Cl_2, 298 K): δ = 9.56 (br s, 2H, H^2 C_6H_4), 8.38 (d, $J_{H,H}$ = 7.6 Hz, 4H, H^{4,6} C_6H_4), 7.63 (t, $J_{H,H}$ = 7.6 Hz, 2H, H^5 C_6H_4), 4.57 (m, 12H, OCH_2, C*H*^{i}Pr), 2.31 (br s, 4H, C*H*Me$_2$), 1.08 (d, $J_{H,H}$ = 6.9 Hz, 12H, CH*Me*$_2$), 1.02 (d, $J_{H,H}$ = 6.8 Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (75.45 MHz, CD_2Cl_2, 298 K): δ = 163.9 (s, OCN), 131.5 (s, C^{1,3} C_6H_4), 128.9 (s, C^{4,6} C_6H_4), 125.5 (s, C^{2,5} C_6H_4), 71.9 (s, *C*H^{i}Pr), 69.9 (s, OCH_2), 31.2 (s, *C*HMe$_2$), 18.3, 16.1 (2*s*, *C*HMe$_2$).

2.2.2. [Cu$_4$Br$_4$(κ^2-N,N-^{i}Pr-pheboxH)$_2$] (**2**)

Yield: 88% (0.190 g). Color: yellow. *Anal.* Calc. for $C_{36}H_{48}N_4O_4Cu_4Br_4 \cdot CH_2Cl_2$: C, 35.28; H, 4.00; N, 4.45. Found: C, 35.20; H, 4.08; N, 4.37. Molar conductivity (nitromethane, 293 K, S·cm^2·mol^{-1}): 11.6. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ = 10.54 (br s, 2H, H^2 C_6H_4), 8.06 (br s, 4H, H^{4,6} C_6H_4), 7.55 (m, 2H, H^5 C_6H_4), 4.51 (m, 12H, OCH_2, C*H*^{i}Pr), 2.74 (br s, 4H, C*H*Me$_2$), 0.96 (m, 24H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (75.45 MHz, CD_2Cl_2, 298 K): δ = 164.1 (s, OCN), 132.1 (s, C^{1,3} C_6H_4), 129.6 (s, C^{4,6} C_6H_4), 126.7 (s, C^{2,5} C_6H_4), 72.3 (s, *C*H^{i}Pr), 70.5 (s, OCH_2), 31.6 (s, *C*HMe$_2$), 18.1, 16.8 (2*s*, CH*Me*$_2$).

2.2.3. [Cu$_4$I$_4$(κ^2-N,N-^{i}Pr-pheboxH)$_2$] (**3**)

Yield: 90% (0.223 g). Color: yellow. *Anal.* Calc. for $C_{36}H_{48}N_4O_4Cu_4I_4 \cdot CH_2Cl_2$: C, 30.70; H, 3.48; N, 3.87. Found: C, 30.64; H, 3.5; N; 3.88. Molar conductivity (nitromethane, 293 K, S·cm^2·mol^{-1}): 9.1. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ = 10.28 (br s, 2H, H^2 C_6H_4), 8.00 (d, $J_{H,H}$ = 7.6 Hz, 4H, H^{4,6} C_6H_4), 7.54 (t, $J_{H,H}$ = 7.6 Hz, 2H, H^5 C_6H_4), 4.46 (m, 12H, OCH_2, C*H*^{i}Pr), 2.68 (br s, 4H, C*H*Me$_2$), 0.98 (d, $J_{H,H}$ = 7.2 Hz, 12H, CH*Me*$_2$), 0.90 (d, $J_{H,H}$ = 6.8 Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 298 K): δ = 163.7 (s, OCN), 132.7 (s, C^{1,3} C_6H_4), 129.9 (s, C^{4,6} C_6H_4), 126.9 (s, C^{2,5} C_6H_4), 72.9 (s, *C*H^{i}Pr), 70.2 (s, OCH_2), 31.7 (s, *C*HMe$_2$), 18.8, 15.9 (2*s*, CH*Me*$_2$).

2.3. Synthesis and characterization of complex [Cu$_4$I$_4$(κ^2-N,N-^{i}Pr-pheboxH)$_2$]$_n$ (**4**)

To a solution of (*S*,*S*)-^{i}Pr-pheboxH (0.051 g, 0.173 mmol) in dichloromethane (15 mL), CuI (0.049 g, 0.259 mmol) was added and the mixture stirred at room temperature during 24 h. Then, the reaction mixture was filtered via cannula and concentrated under reduced pressure to *ca.* 2 mL and diethyl ether/*n*-hexane (1:2) (30 mL) was added. The resulting dark yellow solid was washed with *n*-hexane (3 × 5 mL) and vacuum-dried. Yield: 96% (0.250 g). Color: dark-yellow. Molar conductivity (nitromethane, 293 K, S·cm^2·mol^{-1}): 19.3. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ = 8.97 (br s, 2H, H^2 C_6H_4), 8.08 (d, $J_{H,H}$ = 7.6 Hz, 4H, H^{4,6} C_6H_4), 7.57 (t, $J_{H,H}$ = 7.6 Hz, 2H, H^5 C_6H_4), 4.53 (m, 4H, OCH_2), 4.31–4.19 (2*m*, 8H, OCH_2, C*H*^{i}Pr), 2.06 (br s, 4H, C*H*Me$_2$), 1.01 (d, $J_{H,H}$ = 6.8 Hz, 12H, CH*Me*$_2$), 0.94 (d, $J_{H,H}$ = 6.8 Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (75.45 MHz, CD_2Cl_2, 298 K): δ = 162.9 (s, OCN), 130.4 (s, C^{1,3} C_6H_4), 128.2 (s, C^{4,6} C_6H_4), 126.3, 126.2 (2*s*, C^{2,5} C_6H_4), 71.2 (s, OCH_2), 69.4 (s, *C*H^{i}Pr), 32.2 (s, *C*HMe$_2$), 17.8, 16.5 (2*s*, *C*HMe$_2$).

2.4. Synthesis and characterization of complex {[Cu(κ^2-N,N-^{i}Pr-pheboxH)][BF$_4$]}$_n$ (**5**)

To a solution of (*S*,*S*)-^{i}Pr-pheboxH (0.052 g, 0.173 mmol) in tetrahydrofuran (15 mL), the complex $[Cu(MeCN)_4][BF_4]$ (0.054 g, 0.173 mmol) was added and the mixture stirred at room temperature during 1 h. The solvent was then evaporated under reduced pressure, the solid residue was dissolved in dichloromethane and the resulting solution filtered via cannula. Then, the solution obtained was concentrated under reduced pressure to *ca.* 2 mL and diethyl ether (30 mL) was added giving a white solid which was washed with diethyl ether (3 × 5 mL) and vacuum-dried. Yield: 82% (0.064 g). Color: White. *Anal.* Calc. for $C_{18}H_{24}BCuF_4N_2O_2$: C, 47.96; H, 5.37; N, 6.21. Found: C, 47.64; H, 5.89; N, 6.30. MS-FAB: *m*/*z* = 663.75 [Cu(^{i}Pr-pheboxH)$_2$]$^+$, 363.32 [Cu(^{i}Pr-pheboxH)]$^+$. IR (KBr): ν 1063 (BF_4^-) (vs). Molar conductivity (nitromethane, 293 K, S·cm^2·mol^{-1}): 64, (acetone, 293 K, S·cm^2·mol^{-1}): 117. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ = 8.73 (br s, 1H, H^2 C_6H_4), 8.12 (m, 2H, H^{4,6} C_6H_4), 7.50 (m, 1H, H^5 C_6H_4), 4.93 (m, 2H, OCH_2), 4.57 (m, 4H, OCH_2, C*H*^{i}Pr), 1.99 (m, 2H, C*H*Me$_2$), 1.06 (m, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (100.61 MHz, CD_2Cl_2, 298 K): δ = 170.3 (s, OCN), 133.1 (s, C^{4,6} C_6H_4), 130.4 (s, C^5 C_6H_4), 127.5 (s, C^2 C_6H_4), 126.5 (s, C^{1,3} C_6H_4), 73.3 (s, OCH_2), 70.7 (s, *C*H^{i}Pr), 32.2 (s, *C*HMe$_2$), 18.2, 17.4 (2*s*, CH*Me*$_2$).

2.5. Synthesis and characterization of complex [Cu$_2$(CF$_3$SO$_3$)$_2$(κ^2-N,N-^{i}Pr-pheboxH)]$_n$ (**6**)

To a solution of (*S*,*S*)-^{i}Pr-pheboxH (0.052 g, 0.173 mmol) in dichloromethane (15 mL), the compound $2Cu(CF_3SO_3) \cdot C_7H_8$ (0.090 g, 0.173 mmol) was added and the mixture stirred at room temperature during 24 h. Then, the reaction mixture was filtered via cannula, concentrated under reduced pressure to *ca.* 2 mL and diethyl ether/*n*-hexane (1:2) (30 mL) was added. The resulting yellow solid was washed with *n*-hexane (3 × 5 mL) and vacuum-dried. Yield: 88% (0.110 g). Color: yellow. *Anal.* Calc. for $C_{20}H_{24}N_2O_8Cu_2F_6S_2$: C, 33.11; H, 3.33; N, 3.86; S, 8.84. Found: C, 33.41; H, 3.87; N, 4.00; S, 8.64. MS-FAB: *m*/*z* = 575.36 [Cu$_2$(^{i}Pr-pheboxH)(CF$_3$SO$_3$)]$^+$, 363.31 [Cu(^{i}Pr-pheboxH)]$^+$. IR (KBr): ν 1257 (vs), 1160 (s), 1029 (s) (CF_3SO_3) cm^{-1}. Molar conductivity (nitromethane, 293 K, S·cm^2·mol^{-1}): 7, (acetone, 293 K, S·cm^2·mol^{-1}): 92. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 298 K): δ = 9.36 (s, 1H, H^2 C_6H_4), 8.15 (m, 2H, H^{4,6} C_6H_4), 7.60 (m, 1H, H^5 C_6H_4), 4.82 (m, 2H, OCH_2), 4.64 (m, 2H, C*H*^{i}Pr), 4.52 (m, 2H, OCH_2), 1.88 (m, 2H, C*H*Me$_2$), 0.90 (m, 6H, CH*Me*$_2$), 0.86 (m, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR