Polyhedron 122 (2017) 203–209

Contents lists available at ScienceDirect

Polyhedron

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

Synthesis, crystal structure and properties of a pyrimidine modulated tripyridyldiamino ligand and its complexes

Rayyat Huseyn Ismayilov [a], Wen-Zhen Wang [b], Gene-Hsiang Lee [c], Shie-Ming Peng [c], Baghir A. Suleimanov [a,*]

[a] Oil Gas Scientific Research Project Institute, SOCAR, Baku, Azerbaijan
[b] School of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an, Shaanxi, China
[c] Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

ARTICLE INFO

Article history:
Received 8 August 2016
Accepted 5 November 2016
Available online 27 November 2016

Keywords:
Ligand design
Copper complex
Metal–metal interactions
Nickel
Electrochemistry

ABSTRACT

A new pyrimidine-modulated ligand, N^2-(pyridin-2-yl)-N^6-(pyrimidin-2-yl)pyridine-2,6-diamine (H_2pppmda) (**1**), its mononuclear copper(II) complex $[Cu(H_2pppmda)(CH_3OH)](ClO_4)_2$ (**2**) and pentanickel metal string complex $[Ni_5(\mu_5\text{-pppmda})_4Cl_2]$ (**3**) have been synthesized and structurally characterized. X-ray analysis showed that the free ligand exhibits the *syn–anti–syn–syn* conformation and intermolecular hydrogen bonds link the ligand molecules to a 1-D network along the *c* axis. H_2pppmda coordinates to the metal atom with all-anti mode in the copper mononuclear complex **2** and the coordination geometry of the Cu(II) ion is an elongated octahedron. The $[Ni_5(\mu_5\text{-pppmda})_4Cl_2]$ complex involves a Ni_5 linear chain unit where all the Ni–Ni–Ni angles are nearly 179° and which is terminated by the two axial ligands. The pentanuclear linear metal chain is helically wrapped by four *syn–syn–syn–syn* type pppmda^{2-} ligands. There are two types of Ni–Ni distance in this complex. Terminal Ni–Ni distances bonded with the axial ligand are longer (2.3669(8) Å); the inner Ni–Ni distances are short at 2.2987(6) Å. The terminal Ni(II) ions bonded with the axial ligands are square-pyramidal (NiN_4Cl) with long Ni–N_{av} bonds (2.096 Å), consistent with a high-spin Ni(II) configuration. The inner three Ni(II) ions have short Ni–N_{av} bond distances (1.902(4)–1.888(4) Å), consistent with a square planar (NiN_4), diamagnetic arrangement of a low-spin Ni(II) configuration. This compound exhibits magnetic behavior similar to $[Ni_5(\mu_5\text{-tpda})_4Cl_2]$, indicating an antiferromagnetic interaction of the two terminal high-spin Ni(II) ions. Electrochemical studies showed that the pentanickel(II) complex can undergo one reversible oxidation at +0.76 V. The introduction of an electron-withdrawing pyrimidine ring to the spacer ligand retarded the oxidation of the pentanickel metal string and stabilized the complex.

1. Introduction

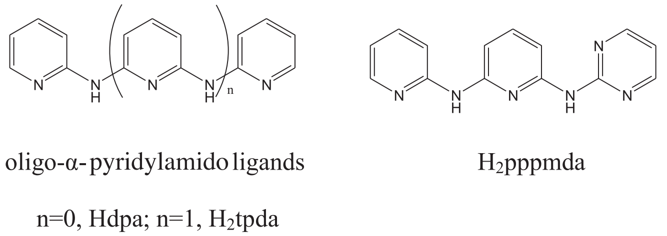
Metal string complexes (EMAC – Extended metal atom chain) are very important for a fundamental understanding of metal–metal interactions and in potential applications such as a molecular metal wires and switches [1]. A series of tri- [2], tetra- [3], penta-[4], hexa- [5], hepta- [6], nonanuclear- [7] and undecanuclear [8] metal string complexes of Cu, Ni, Co, Cr, Ru and Rh with oligo-α-pyridylamido ligands have been synthesized and structurally characterized (Scheme 1).

The typical structure of this family includes a linear metal chain, which is helically wrapped by four deprotonated oligo-α-pyridylamido ligands; all the pyridine nitrogen and amido nitrogen atoms are coordinated to the metal centers in the *syn* form. The adjacent pyridyl rings are not coplanar due to the repulsion of the β-H atoms, and the dihedral angle between adjacent pyridyl rings is about 45°. Our current research in this field is heading in two directions: (1) extending the length of the molecules. Research in this area is strongly stimulated by the potential application of metal string complexes as molecular wires. Work in this area is hindered by two factors: the synthetic difficulty increases and the yield decreases with the increase in the number of metal atoms and the length of the molecules. It is well known that longer metal string complexes more easily decompose by oxidation [9]; (2) modulating the electronic structures and properties. The electronic structure of metal string complexes depends on both the metal and the ligands. Previous research on metal string of oligo-α-pyridylamido ligands has revealed that in nickel string no nickel-nickel

---

* Corresponding author.
E-mail address: Baghir.Suleymanov@socar.az (B.A. Suleimanov).

http://dx.doi.org/10.1016/j.poly.2016.11.023
0277-5387/© 2016 Published by Elsevier Ltd.



Scheme 1. Oligo-α-pyridylamine and pyrimidine-modulated oligo-α-pyridylamine ligands.

bonds are observed between the nickel atoms [4f,4d]. Cobalt and chromium string complexes, however, showed significant metal–metal interactions and higher electronic conductivities than those of nickel strings [1b,6c]. Although there are no bonds between the nickel atoms in the nickel metal string complexes, they are still of great interest because of their stability and ability to be synthesized in high yields.

Recently we designed a series of new ligands, pyrazine-modulated oligo-α-pyridylamino ligands, by including pyrazine instead of pyridine ring(s) in the oligo-α-pyridylamino ligands [2e,6c,7b]. The introduction of one or more nitrogen-rich aromatic ring, pyrazine, to the ligand significantly improves the reactivity, leading to metal strings, and the products are more resistant to oxidation than the corresponding oligo-α-pyridylamino metal string complexes. By using the tuning ligands, we have succeeded in not only synthesizing the longest metal strings so far obtained, such as nonachromium and heptacobalt metal string complexes, but also in synthesizing many new metal strings with properties different from those of the oligo-α-pyridylamido ligand metal strings.

Here we report for the first time the syntheses of the novel pyrimidine-modulated ligand N^2-(pyridin-2-yl)-N^6-(pyrimidin-2-yl)pyridine-2,6-diamine (H_2pppmda) (**1**), its copper complex [Cu(H_2pppmda)(CH_3OH)]$(ClO_4)_2$ (**2**) and its metal string complex [Ni_5(μ_5-pppmda)$_4Cl_2$] $2CHCl_3$ CH_2Cl_2 (**3** $2CHCl_3$ CH_2Cl_2).

2. Experimental

2.1. Materials

All reagents and solvents were obtained from commercial sources and were used without further purification, unless otherwise noted. The preparation of the starting material (6-bromo-2-pyridyl)(2′-pyridyl)amine was carried out according to the literature [10]. 2-Aminopyrimidine was supplied by Sigma Aldrich (purity 97%). The solvent CH_2Cl_2 was dried over CaH_2 and freshly distilled prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized twice from ethyl acetate and dried under vacuum.

2.2. Physical measurements

Absorption spectra were recorded on a HEWLETT PACKARD 8453 spectrophotometer. IR spectra were performed with a Perkin Elmer FT–IR spectrometer PARAGON1000 in the range 400–4000 cm^{-1}. Elemental analyses were carried out on a FlashEA 1112 Series CHNS-O analyzer. ^1H NMR spectra were recorded in $(CD_3)_2SO$ and chemical shifts were reported in ppm relative to $(CD_3)_2SO$ (δ 2.49 ppm for 1H). FAB-MS mass spectra were obtained with a JEOL JMS-700 HF double focusing spectrometer operating in the positive ion detection mode. The molar magnetic susceptibility was recorded in the range 5–300 K on a SQUID system with a 2000 G external magnetic field. Electrochemistry was performed with a three-electrode potentiostat (CH Instruments, Model 750A) in a CH_2Cl_2 solution deoxygenated by purging with pre-purified nitrogen gas. Cyclic voltammetry was conducted with a three-electrode cell equipped with a BAS glassy carbon (0.07 cm^2) or platinum (0.02 cm^2) disk as the working electrode, a platinum wire as the auxiliary electrode and a home-made Ag/AgCl (saturated) reference electrode. The reference electrode was separated from the bulk solution by a double junction filled with an electrolyte solution. Potentials are reported *versus* Ag/AgCl (saturated) and referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple, which occurs at $E_{1/2}$ = +0.54 V *versus* Ag/AgCl (saturated). The working electrode was polished with 0.03 μm aluminium on Buehler felt pads and was put under ultrasonic radiation for 1 min prior to each experiment. The reproducibility of individual potential values was within ±5 mV.

2.3. Preparation of the compounds

2.3.1. N^2-(pyridin-2-yl)-N^6-(pyrimidin-2-yl) pyridine-2,6-diamine (H_2pppmda) (**1**)

The reaction of (6-bromo-2-pyridyl)(2′-pyridyl)amine (10.0 g, 0.040 mol) and 2-aminopyrimidine (4.56 g, 0.048 mol) in the presence of $Pd_2(dba)_3$ (0.732 g, 2 mol%), BINAP (0.996 g, 4 mol%) and Bu^tONa (6.54 g, 0.068 mol) in benzene (250 mL) for 72 h gave the crude product **1**. Purification by column chromatography over silica gel with dichloromethane–acetone (5:1) as the eluent gave colorless crystals of **1** after evaporation (8.42 g, 80% yield); M.p.: 206 °C; IR (KBr) ν/cm^{-1}: 3184 w (NH), 3097 w, 3030 w (Ar CH), 1568 s, 1546 m, 1449 s, 1435 s, 1422 s (Ar), 1308 s, 1234 m, 1160 s, 1102 m, 894 m, 796 m, 768 m, 733 m, 672 w; UV/Vis (CH_3OH) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 256 ($2.67 \times 10^4$), 326 ($2.31 \times 10^4$); ^1H NMR (400 MHz, $(CD_3)_2SO$) δ (ppm): 8.50 (s, 1H, –NH), 8.66 (s, 1H, –NH), 7.63 (d, *J* = 4.8 Hz, 2H, Ar–H), 7.42 (d, *J* = 8.4 Hz, 1H, Ar–H), 7.26 (d, *J* = 4.4 Hz, 1H, Ar–H), 6.75–6.62 (m, 3H, Ar–H), 6.07 (d, *J* = 8.0 Hz, 1H, Ar–H), 6.00 (t, *J* = 9.2 Hz, 1H, Ar–H), 5.93 (t, *J* = 6.4 Hz, 1H, Ar–H); MS (FAB): *m/z* (%): 265(100) $[M]^+$; elemental analysis (%) $C_{14}H_{12}N_6$ calc.: C 63.62, H 4.58, N 31.80; found: C 63.68, H 4.42, N 31.64.

2.3.2. [Cu(H_2pppmda)(CH_3OH)]$(ClO_4)_2$ (**2**)

A mixture of H_2pppmda (0.100 g, 0.38 mmol) and $Cu(ClO_4)_2\cdot 6H_2O$ (0.163 g, 0.44 mmol) in methanol (60 mL) was stirred overnight. The solution was then filtered to remove insoluble impurities and concentrated under vacuum. Diffusing ether into the CH_3OH solution provided blue single crystals suitable for X-ray analysis (0.138 g, 65% yield). IR (KBr) ν/cm^{-1}: 3448 w, 3300 w (OH), 3251 w, 3211 w (NH), 3072 s (Ar CH), 1650 s, 1624 s, 1561 s, 1490 s,1467 s, 1448 s, 1409 s, 1422 m (Ar), 1300 w, 1215 m, 1087 s (ClO_4^-), 1041 m, 1017 w, 813 w, 795 m, 779 s, 763 s, 691 w, 636 s, 520; UV/Vis (CH_3OH) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 208 ($3.85 \times 10^4$), 238 ($3.32 \times 10^4$), 310 ($2.62 \times 10^4$), 334 ($3.98 \times 104$), 454 (69.81), 654 (23.82); elemental analysis (%)$C_{15}H_{16}Cl_2CuN_6O_9$ calc.: C 32.24, H 2.89, N 15.04; found: C 32.31, H 2.97, N 15.19.

2.3.3. [Ni_5(μ_5-pppmda)$_4Cl_2$] (**3**)

Anhydrous $NiCl_2$ (0.78 g, 6.00 mmol), H_2pppmda (1.06 g, 4.00 mmol) and naphthalene (40 g) were placed in an Erlenmeyer flask. The mixture was heated (about 180–190 °C) for 15 h under argon and then a solution of potassium *tert*-butoxide (1.00 g, 8.91 mmol) in *n*-butyl alcohol (5 mL) was added dropwise. The mixture was refluxed for 8 h continuously. After the mixture had cooled, hexane was added to wash out naphthalene and then 200 ml of CH_2Cl_2 was used to extract the complex. A dark brown-purple complex was obtained after evaporation. Single crystals suitable for X-ray diffraction were obtained from diffusion