Asian Journal of Chemistry; Vol. 27, No. 11 (2015), 4141-4144

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.19135

Template Synthesis and Spectral Characterization of New Lead(II)-Schiff Base Macrocyclic Complexes Incorporating Phenanthroline and/or Bipyridine Units

N. Beynek*, N. Tan and H. Beynek

Department of Chemistry, Faculty of Science, Trakya University, Edirne, Turkey

*Corresponding author: Fax: +90 284 2351198; Tel: +90 284 2359592/1228; E-mail: nesrinbeynek@yahoo.co.uk

Received: 27 February 2015; *Accepted*: 9 April 2015; *Published online*: 16 July 2015; AJC-17421

Lead(II) complexes of Schiff-bases containing phenanthroline and/or bipyridine units were synthesized by the template reaction between new diamine compound, 6,6'-*bis*(2-aminophenoxymethyl)-2,2'-bipyridine and 2,2-bipyridine-6,6-dicarboxaldehyde or 1,10-phenanthroline-2,9-dicarboxaldehyde in the presence of metal ions. These complexes, [Pb**L1**]$(ClO_4)_2$and [Pb**L2**]$(NO_3)_2$, were characterized and investigated by using; MALDI-TOF and Q-TOF-MS spectroscopy, FTIR, UV/Visible spectroscopy, ^{1}H NMR, Elemental analyses (CHN), magnetic susceptibility and molar conductivity measurements.

Keywords: Template reactions, Schiff base, Bipyridine, Phenanthroline, Macrocyclic complex, Lead(II).

INTRODUCTION

As one of the most important fields in macrocyclic and supramolecular chemistry, Schiff-base macrocycles have been widely and thoroughly studied. In many Schiff base macrocyclization process, reaction products were easily obtained in high yields with using metal template[1-5]. Recently, we have synthesized and characterized some acyclic and macrocyclic Schiff base complexes using template methods and studied their cytotoxic activities[6-8]. The templated heavy metal ion chemistry of mixed donor Schiff base macrocycles has also received considerable attention by us[6-8] and others[9-11]. The heavy metal complexes containing macrocyclic or acyclic ligands have been used as extractants or sensors of these metals for recycling, biological, or environmental purposes[2-4,8-11]. These metal complexes also seem to be more interesting from a structural point of view because of the ability of these cations to modify both coordination numbers and geometries. Here, we describe the synthesis of Pb(II) complexes of Schiff-bases containing phenanthroline and/or bipyridine units by the template reaction between new diamine compound, 6,6'-*bis*(2-aminophenoxymethyl)-2,2'-bipyridine and 2,2-bipyridine-6,6-dicarboxaldehyde or 1,10-phenanthroline-2,9-dicarboxaldehyde in the presence of metal ions. New diamine compound and Schiff base complexes, [Pb**L1**]$(ClO_4)_2$ and [Pb**L2**]$(NO_3)_2$, were characterized by using; MALDI-TOF andQ-TOF-MS mass spectroscopy, FAR-FT-IR, UV/visible spectroscopy, ^{1}H NMR, elemental analyses (CHN), magnetic susceptibility and molar conductivity measurements.

EXPERIMENTAL

6,6'-*Bis*(bromomethyl)-2,2'-bipyridine[12], 2,2'-bipyridine-6,6'-dicarboxaldehyde[8] and 1,10-phenanthroline-2,9-dicarboxaldehyde[13] were synthesized according to published procedures. All other chemicals were purchased from Merck or Aldrich and were used withoutfurther purification.

Melting points were determined using an Gallenkamp MPD350.BM2.5 digital melting point apparatus and were uncorrected. The compounds were checked for purity by TLC on silica gel 60 F254 (Merck).Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Frontier FAR-FT-IR spectrometer, fitted with an GladiATR platform, at 4000-400 cm^{-1}; ^{1}H NMR spectra were recorded with a Varian (300 MHz) in $CDCl_3$ or acetone-d_6 as solvent. ^{13}C NMR spectra were recorded with a Varian spectrometer at 75.5 MHz in $CDCl_3$ as solvent. Chemical shifts are reported as δ values in parts per million (ppm). Positive ion and linear mode MALDI-MS of the complexes were obtained no matrix using a Bruker Microflex LT MALDI-TOF and Q-TOF MS AB-SCIEX Triple TOF 4600 System mass spectrometer.Elemental analyses were performed on a CHNS-O Thermo Finnigan Flash EA1112 elemental analyser. Electronic spectra was recorded at room temperature on a Schimadzu UV-1700 Pharma spectrophotometer, using 1 cm quartz cuvettes and DMSO as solvent. Molar conductance was measured using a WTW Inolab Thermal 720P conductivitymeter where the cell constant was calibrated with 0.001 M KCl solution and acetone was used as solvent. Solid-state magnetic susceptibility data were collected on a powdered microcrystalline sample using a Sherwood Scientific Magnetic Susceptibility Balance at room temperature.

Synthesis

6,6'-*Bis*(2-nitrophenoxymethyl) 2,2'-bipyridine: The new precursor dinitro compound was prepared using 6,6'-*bis*(bromomethyl)-2,2'-bipyridine and potassium *o*-nitrophenolate by a modification procedure to that described previously published methods[14]. A solution of 2-nitrophenol (1.392 g, 10 mmol) in hot anhydrous DMF (40 mL) was treated with K_2CO_3 (0.690 g, 5 mmol) and gently boiled. To this solution, 6,6'-*bis*(bromomethyl)-2,2'-bipyridine (1,710 g, 5 mmol) in 20 mL anhydrous DMF was added during 0.5 h. Gently reflux was maintained for 4 h and a half of the solvent was distilled from the mixture, which was then poured into H_2O (400 mL). Yellow product was filtered off and washed with dilute aq. NaOH solution and H_2O and then dried. Yield: 2.213 g (96.6 %). m.p. 182-183 °C. IR (KBr, ν_{max}, cm^{-1}): 3079w, 2905w, 2856w, 1611m, 1584m, 1574m, 1521vs, 1491m, 1443s, 1404w, 1351s (NO_2), 1294s, 1270m, 1257s, 1157m, 1108m, 1087m, 1048m, 993m, 861s (NO_2), 819m, 785s, 766m, 744vs, 679m, 632s, 525w, 479w. ^1H NMR (300 MHz; $CDCl_3$): δ 5.44 (4H, s, CH_2), 7.1 (2H, t, J = 7.91 Hz), 7.2 (2H, d, J = 7.3 Hz), 7.53 (2H, d, J = 7.3 Hz), 7.71 (2H, d, J = 7.3 Hz), 7.88-7.94 (4H, m), 8.34 (2H, d, J = 7.9 Hz). ^{13}C NMR (75 MHz; $CDCl_3$): δ 71.82 (CH_2), 114.89, 120.51, 121.04, 121.51, 125.97, 134.30, 137.59, 140.35 (C), 152.33 (C), 155.51 (C), 155.70 (C).

6,6'-*Bis*(2-aminophenoxymethyl)-2,2'-bipyridine: Reduction of the above dinitro derivative,6,6'-*bis*(2-nitrophenoxymethyl)-2,2'-bipyridine, to the diamine compound was effected by modification of a previously reported method[14]. 6,6'-*Bis*(2-nitrophenoxymethyl)-2,2'-bipyridine (1.832 g, 4 mmol) was slurried in EtOH-H_2O (1:1, 80 mL) containing iron powder (2.234 g, 40 mmol) and brought to reflux. Glacial acetic acid (1.2 mL) was added dropwise and reflux was maintained for a further 18 h after which the mixture was filtered hot (using well packed celite aid). The cooled fitrate was extracted with chloroform and oily product was obtained by evaporation of organic phase under vacuum. Crystallization from EtOH:H_2O (1:1, 20 mL) gave the pale brown powder product in 70 % (1.103 g) yield. m.p. 180-182 °C. IR (KBr, ν_{max}, cm^{-1}): 3439m (NH_2), 3356m δ(NH_2),1612m, 1572m, 1505vs, 1442s, 1403w, 1279w,1267m, 1218vs, 1140w, 1108w, 1081vw, 1048m, 991m, 908w, 849w, 782vs, 734vs, 659w, 631s, 548s. ^1H NMR (300 MHz; $CDCl_3$): δ 3.90 (4H, s (br), NH_2), 5.26 (4H, s, CH_2), 6.60-6.83 (8H, m), 7.45 (2H, d, J = 7.7Hz), 7.78 (2H, t, J = 7.8 Hz), 8.30 (2H, d, J = 7.9 Hz). ^{13}C NMR (75 MHz; $CDCl_3$): δ 71.46 (CH_2), 112.61, 115.65, 118.69, 120.34, 121.45, 122.0, 124.07, 136.67 (C), 137.96 (C), 154.87(C), 155.76(C). Q-TOF (*m/z*): Found 399.1833 calc.: (399.1800)for $[M+H]^+$.

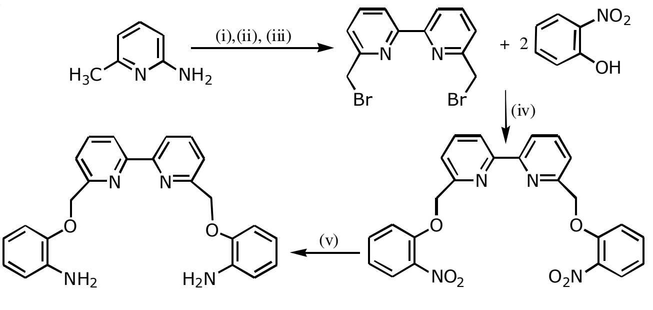
Macrocyclic Schiff base complexes: 2,2'-Bipyridine-6,6'-dicarboxaldehyde or 1,10-phenanthroline-2,9-dicarboxaldehyde (1.0 mmol) was dissolved in MeOH (25 mL) containing $Pb(ClO_4)_2 \cdot H_2O$ or $Pb(NO_3)_2$ (1.0 mmol). The solution was stirred vigorously and heated while a methanolic solution of 6,6'-*bis*(2-aminophenoxymethyl)-2,2'-bipyridine (0.40 g, 1.0 mmol) was added slowly. The resultant solution was refluxed for 4-5 h and filtered hot. The solvent of the reaction mixture was reduced to half its original volume and then the mixture was placed in a refrigerator to induce precipitation. The yellow powder products were filtered and dried. Yields 70 and 50 % respectively.

[Pb**L1**]$(ClO_4)_2$ (ν_{max}, cm^{-1}):1632m (C=N), 1586m, 1490m, 1441m, 1373w, 1262m, 1213m, 1183w, 1080vs (ClO_4^-), 1005m, 911w, 795s, 756m, 743s, 622s (ClO_4^-), 582w, 524w. ^1H NMR (300 MHz; acetone-d_6): δ5.80 (4H, s, CH_2), 6.93 (2H, d, J = 7.9 Hz), 7.16 (2H, t, J = 7.1 Hz), 7.28-7.49 (4H, m), 7.68 (2H, t, J = 7.8 Hz), 7.81 (2H, d, J = 7.9 Hz), 7.87 (2H, d, J = 7.5 Hz), 8.36 (2H, d, J = 7.6 Hz), 8.68 (2H, t, J = 7.9 Hz), 8.93 (2H, d, J = 8.3 Hz), 9.40 (2H, s, HC=N). Λ_M (μS/cm), (acetone, 10^{-3} M): 160, 25.4 °C. μ_{eff} (BM), 24 °C: 0.88 BM. UV-visible (DMSO): 305 nm $\pi \rightarrow \pi^*$ (C=N), 292 nm $\pi \rightarrow \pi^*$ (aromatik ring). MALDI-TOF (*m/z*): Found: 781.788, calc.: 781.828 for $[Pb(\mathbf{L1})]^+$. Found: C, 44.67; H, 3.14; N, 8.53. Calcd. for $C_{36}H_{26}N_6O_{10}Cl_2Pb$: C, 44.09; H, 2.67; N, 8.57.

[Pb**L2**]$(NO_3)_2$ (ν_{max}, cm^{-1}): 1607m (C=N), 1584m, 1505m, 1488m, 1440m, 1366s (NO_3^-), 1294vs,1210s, 1117m, 1029m, 991m, 921w, 868s(NO_3^-), 794s, 754vs, 649m, 589m. Λ_M (μS/cm),(acetone,10^{-3} M): 178, 24.2°C μ_{eff}(BM), 24 °C: 0.99 BM. UV-visible (DMSO): 310 nm $\pi \rightarrow \pi^*$(C=N), 290, 286 nm $\pi \rightarrow \pi^*$ (aromatic ring). MALDI-TOF (*m/z*): Found: 805,745 calc.: 805.850 for $[Pb(\mathbf{L2})]^+$. Found: C, 49.03; H, 2.80; N, 11.85. Calcd. for $C_{38}H_{26}N_8O_8Pb$: C, 49.08; H, 2.82; N, 12.05.

RESULTS AND DISCUSSION

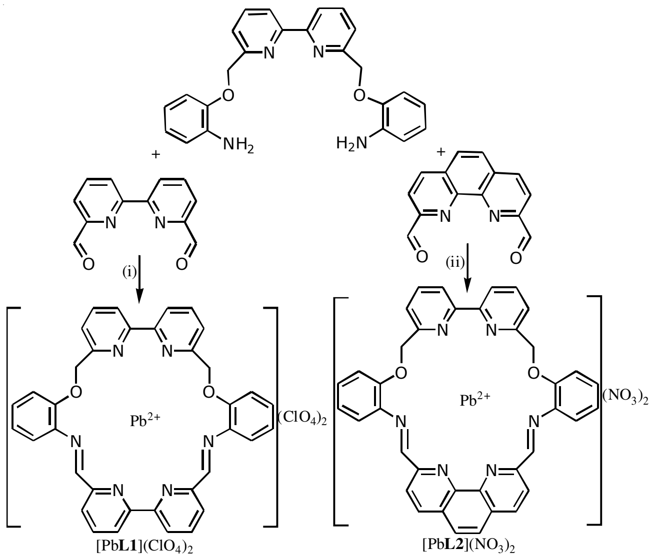
The new diamino compound, 6,6'-*bis*(2-aminophenoxymethyl)-2,2'-bipyridine was obtained starting from 6-amino-2-methylpyridine, which was converted to 6-bromo-2-methylpyridine by reaction with concentrated aqueous hydrobromic acid and bromine. Then, 6,6'-dimethyl-2,2'-bipyridine was prepared using 6-bromo-2-methylpyridine by a modification of the method described by Iyoda *et al.*[15] and was reacted with N-bromosuccinimide. Then, the dinitro compound, 6,6'-*bis*(2-nitrophenoxymethyl) 2,2'-bipyridine, was prepared using a Williamson ether synthesis from two equivalents of 2-nitrophenol and one equivalent of 6,6'-*bis*(bromomethyl)-2,2'-bipyridine in DMF and nitro groups were reduced to amine using metallic iron[14] (**Scheme-I**). Physical data for all compounds are given in the experimental section. The complexes were obtained with 50-70 % yields.



(i) 47% HBr, Br_2, $NaNO_2$ then NaOH **(ii)** $NiCl_2(PPh_3)_2$, Zn, Et_4NI, THF, under Ar **(iii)** NBS, CCl_4, benzoyl peroxide **(iv)** DMF, K_2CO_3 **(v)** Fe, CH_3COOH.

Scheme-I: Synthetic route for diamine compound, 6,6'-*bis*(2-aminophenoxymethyl)-2,2'-bipyridine

Two new lead(II) complexes of the 23-membered Schiff base macrocyclic ligands **L1** and **L2** were prepared using *in* *situ* metal-template condensations of 6,6'-*bis*(2-aminophenoxymethyl)-2,2'-bipyridine with 2,2'-bipyridine-6,6'-dicarboxaldehyde or 1,10-phenanthroline-2,9-dicarboxaldehyde (**Scheme-II**). Condensation reactions attempted at normal and high dilutions in the absence of metal ion resulted in obtaining cream sticky solid of indefinite composition presumably containing polymeric species. The dialdehyde compound, 2,2'-bipyridine-6,6'-dicarboxaldehyde, was synthesized to our previous report[8] and the other dialdehyde compound, 1,10-phenanthroline-2,9-dicarboxaldehyde, was prepared by reaction of 2,9-dimethyl-1,10-phenanthroline (neocuproine) with selenium dioxide by adaptation of the procedure of Chandler *et al.*[13].



(i) $Pb(ClO_4)_2$, MeOH (ii) $Pb(NO_3)_2$, MeOH.

Scheme-II: Synthetic route for the complexes, [Pb**L1**]$(ClO_4)_2$ and [Pb**L2**]$(NO_3)_2$

The most important infrared bands for the complexes together with their assignments are given in the experimental section. The infrared spectra of Pb(II) metal complexes of **L1** and **L2** in the region of 4000-400 cm^{-1} show a strong absorption band 1632 and 1607 cm^{-1}, respectively, which is assigned to the ν(C=N) streching vibration, indicating the formation of the Schiff-base products. Furthermore, the absence of ν(C=O) and ν(N-H) streching vibrations in the spectra of the complexes, as compared to the aldehyde and diamine, respectively, further indicate the formation of the Schiff base. The imine band for the complex of **L2** (1607 cm^{-1}) is lower than for **L1** (1632 cm^{-1}) but is consistent with a degree of extended delocalisation in **L2** involving the phenanthroline parts of the macrocycle[14]. The bands at approximately 1586 and 1490 cm^{-1} associated with $\nu(C=N)_{py}$ and ν(C=C) vibrations from the pyridine and phenyl rings[16]. For the [Pb**L1**]$(ClO_4)_2$ complex absorptions at 1080 and 621 cm^{-1} (respectively very strong and strong) were assigned to the ν_3 and ν_4 streching modes of the tetrahedral ionic perchlorate[17].The unsplit nature of these bands indicates that the anions are not coordinated. The strong and sharp bands at 1366 and 861 cm^{-1} are characteristic of ionic nitrate for [Pb**L2**]$(NO_3)_2$ complex[17].These results suggest that the perchlorate and nitrate anions are not coordinated to the metal ions in solution, reflecting the weak coordination ability of these anions.

The molar conductance values for the lead(II) complexes, measured in acetone at 24.5 °C are in the range characteristic of 2:1 electrolytes[18]. These results are supported by the IR spectra of these complexes.

The composition of the complexes was particularly confirmed by MALDI-TOF mass spectrometry. In the mass spectrum of complexes [Pb**L1**]$(ClO_4)_2$ and [Pb**L2**]$(NO_3)_2$ were observed corresponding to the positive ions $[Pb(\mathbf{L1})]^+$ and $[Pb(\mathbf{L2})]^+$ [(found: 781.788 calc.: 781.828 and found: 805.745 (calc.: 805.850)] respectively as accurate mass. Each of the complexes had a 1:1:1 (dialdehyde:diamine:metal) stoichiometry. The formula is in agreement with the mass spectral data. Microanalytical data for these complexes also denotes a metal-to-ligand ratio of 1:1.

The proton NMR spectrum of the soluble complex [Pb**L1**]$(ClO_4)_2$ in acetone-d_6 shows 26 peaks, which is consistent with the given structure.The imine protons appear as characteristic most down field singlet (δ 9.40) and attributable to aldehydic and amino functions are noticeably absent. The methylene protons were assigned to the most upfield signal (5.80 ppm) as a singlet in the spectra.

The electronic spectra of the complexes exhibit an intense absorption band in the ranges 290-292 nm which may be assignable to the intra ligand ($\pi \rightarrow \pi^*$) transitions of the conjugated aromatic rings[19]. The complexes has also broad band around 310 nm region, which may be caused by the nitrogen→metal charge transfer (L→M charge transfer).

The magnetic susceptibilities of the solid-state complexes were measured by the Gouy balance method. The magnetic moments of the complexes were measured at room temperature and were found 0.88 BM, for [Pb**L1**]$(ClO_4)_2$ and 0.99 BM for [Pb**L2**]$(NO_3)_2$ consistent with no unpaired electrons in the lead(II) ions. The complexes are found to be diamagnetic as expected for s^2 system.

Conclusion

In the present work, we have reported the synthesis of two new lead(II) complexes of macrocyclic Schiff-bases containing phenanthroline and/or bipyridine units. The cyclocondensation reactions between 6,6'-*bis*(2-aminophenoxymethyl)-2,2'-bipyridine and 2,2-bipyridine-6,6-dicarboxaldehyde or 1,10-phenanthroline-2,9-dicarboxaldehyde in the presence of metal ion yield lead(II) complexes of the Schiff-base macrocycles **L1** and **L2**. The spectroscopic data suggest that **L1** and **L2** are formed as pure macrocyclic metal complexes. The accurate mass of the positive ions, $[Pb(\mathbf{L1})]^+$ and $[Pb(\mathbf{L2})]^+$, have been confirmed by MALDI-TOF mass spectra studies. Each of the complexes had a 1:1:1 (dialdehyde: diamine:metal) stoichiometry. The IR data of both the lead(II) complexes of Schiff bases showed that the **L1** and **L2** were uncoordinated to the lead(II) through the counterions (ClO_4^- or NO_3^-). The composition of the complexes was also confirmed by molar conductivity measurement and ^{1}H NMR spectrometry.

ACKNOWLEDGEMENTS

The authors thank Trakya University for financial support under the research grant No. TUBAP-2013/29.

REFERENCES

1. M. Rezaeivala and H. Keypour, *Coord. Chem. Rev.*, **280**, 203 (2014).
2. R.E. Mewis and S.J. Archibald, *Coord. Chem. Rev.*, **254**, 1686 (2010).
3. N.V. Gerbeleu, V. B. Arion, and J. Burgess, Template Synthesis of Macrocyclic Compounds, Wiley-VCH, New York, Vol. 1 and 3 (1999).
4. B. Dietrich, P. Viout and J.M. Lehn, Macrocyclic Chemistry, Aspects of Organic and Inorganic Supramolecular Chemistry,VCH, Weinheim, Vols. 1-2 (1995).
5. L.F. Lindoy, The Chemistry of Macrocyclic Ligand Complexes, Cambridge University Press, Cambridge, p. 21 and 185 (1989).
6. T. Adatia, N. Beynek and B.P. Murphy, *Polyhedron*, **14**, 335 (1995).
7. N. Beynek, M. McPartlin, B.P. Murphy and I.J. Scowen, *Polyhedron*, **17**, 2137 (1998).
8. G. Uluçam, N. Beynek, Z. Seller, G. Akalin, G. Turan and K. Benkli, *Phosphorus, Sulfur and Silicon Rel. Elem.*, **183**, 2237 (2008).
9. A. Bashall, M. McPartlin, B.P. Murphy, H.R. Powell and S. Waikar, *J. Chem. Soc., Dalton Trans.*, 1383 (1994).
10. D. Esteban-Gómez, T. Enríquez-Pérez, R. Ferreirós-Martínez, M. Mato-Iglesias, C. Platas-Iglesias, A. de Blas and T. Rodríguez-Blas, *Eur. J. Inorg. Chem.*, **31**, 5027 (2010).
11. G. Martinez, V.-K. Tanja, K. Rafael, K. Ulrich, T. Thomas and S. Kai, *J. Serb. Chem. Soc.*, **78**, 2115 (2013).
12. N. Beynek, G. Uluçam, K. Benkli and A.T. Koparal, *Helv. Chim. Acta*, **91**, 2089 (2008).
13. C.J. Chandler, L.W. Deady and J.A. Reiss, *J. Heterocycl. Chem.*, **18**, 599 (1981).
14. D.E. Fenton, B.P. Murphy, A.J. Leong, L.F. Lindoy, A. Bashall and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 2543 (1987).
15. M. Iyoda, H. Otsuka, K. Sato, N. Nisato and M. Oda, *Bull. Chem. Soc. Jpn.*, **63**, 80 (1990).
16. N.S. Gill, R.H. Nuttall, D.E. Scaife and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).
17. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley Interscience, edn 5, p. 252 (1997).
18. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
19. E. Pretsch and T. Clerc, Tables of Spectral Data for Structure Determination of Organic Compounds, Springer-Verlag, edn 2 (1989).