

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

### Complexation of (1*Z*, 2*Z*)-*N*'-1-,*N*'-2-dihydroxy-*N*-1-,*N*-2-dipyridin-2-ylethanedimidamide in mono and dinuclear Zn(II), Cd(II), Hg(II) and Sn(IV) complexes

Ali Kakanejadifard<sup>a</sup>; Abedien Zabardasti<sup>a</sup>; Motaleb Ghasemian<sup>a</sup>; Esmail Niknam<sup>a</sup>

<sup>a</sup> Faculty of Science, Department of Chemistry, Lorestan University, Khorramabad, Iran

**To cite this Article** Kakanejadifard, Ali , Zabardasti, Abedien , Ghasemian, Motaleb and Niknam, Esmail(2008) 'Complexation of (1*Z*, 2*Z*)-*N*'-1-,*N*'-2-dihydroxy-*N*-1-,*N*-2-dipyridin-2-ylethanedimidamide in mono and dinuclear Zn(II), Cd(II), Hg(II) and Sn(IV) complexes', *Journal of Coordination Chemistry*, 61: 11, 1820 – 1826

**To link to this Article:** DOI: 10.1080/00958970701621217

**URL:** <http://dx.doi.org/10.1080/00958970701621217>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Complexation of (1*Z*, 2*Z*)-*N'*-1-,*N'*-2-dihydroxy-*N*-1-, *N*-2-dipyridin-2-ylethanedimidamide in mono and dinuclear Zn(II), Cd(II), Hg(II) and Sn(IV) complexes

ALI KAKANEJADIFARD\*, ABEDIEN ZABARDASTI,  
MOTALEB GHASEMIAN and ESMAIEL NIKNAM

Faculty of Science, Department of Chemistry, Lorestan University, Khorramabad, Iran

(Received 2 May 2007; in final form 13 June 2007)

Mononuclear O,O-coordinated complexes  $K_2(MLCl_2)$   $M = Zn(II)$ ,  $Cd(II)$  and dinuclear complexes  $(MZnLCl_2R_2)^x$  along with dinuclear *N,N*-coordinated complexes  $(M'ZnH_2LCl_2R_2)^y$  (where  $M = Zn(II)$ ,  $Cd(II)$ ,  $Hg(II)$  and  $M' = M$  and  $Sn(IV)$ ;  $R = Cl$ ,  $CH_3$ ;  $x = 0, -2$ ;  $y = 0, +2$ ) of *N'*-1-,*N'*-2-dihydroxy-*N*-1-,*N*-2-dipyridin-2-ylethanedimidamide ( $H_2L$ ) have been prepared. All complexes have been characterized by  $^1H$  NMR, IR, EI-mass spectroscopy and elemental microanalysis. These results are in agreement with our prediction for structures of mono and dinuclear complexes of  $H_2L$  and  $L^{-2}$  with  $Zn(II)$  in the gas phase by theoretical studies.

**Keywords:** vic-dioxime; *N,N*-coordination Mono and Dinuclear Complexes; O,O-Coordinated; Complexes

### 1. Introduction

*Vic*-dioximes are easily modified by substitution with various groups; reaction of amines or thiols with (*E,E*)-dichloroglyoxime or cyanogen-di-*N*-oxide yielded various symmetrically substituted diaminoglyoxime or dithioglyoxime derivatives [1–3]. Oximes are widely used in organic [4, 5], inorganic [6–9], bioinorganic [10], pigment [11], analytical [12, 13] and dyes [14]. Metal containing oxime complexes are utilized in medicine; technetium (V) and copper (II) complexes containing vicinal dioxime are currently used as cerebral and myocardial perfusion imaging agents [15–18]. In a preceding article, we reported synthesis and *N,N*-coordination mono and dinuclear complexes of *N'*-1-, *N'*-2-dihydroxy-*N*-1-, *N*-2-dipyridin-2-ylethanedimidamide ( $H_2L$ ) with  $Zn(II)$ ,  $Cd(II)$ ,  $Hg(II)$  in acidic media (figure 1) [19].

We continue to develop coordination chemistry of  $H_2L$ , introducing *N,N* as well as O,O-coordinated complexes of  $H_2L$  with  $Zn(II)$ ,  $Cd(II)$ ,  $Hg(II)$ , and  $Sn(IV)$ .

\*Corresponding author. Email: kakanejadi.a@lu.ac.ir

## 2. Results and discussion

Mononuclear complexes, **1a–c** were prepared from reaction of  $H_2L$  and chloride salts of Zn(II), Cd(II), Hg(II) [19]. Compounds **2–4** were prepared from reaction of **1a–c** with  $Me_2SnCl_2$  in methanol (figure 2). The solubility of these complexes in common organic solvents allowed their full characterization. In the IR spectrum of **2** the O–H, N–H, C=N and N–O stretching vibrations were at 3091–3205, 3326, 1643 and 988, respectively. In the  $^1H$  NMR of **2** the  $D_2O$  exchangeable protons of OH and NH groups appeared as two singlets at  $\delta = 13.38$  and 12.41 ppm, respectively. In the  $^{13}C$  NMR spectrum of **2** the carbon resonance of oxime groups is found at higher field ( $\delta = 150.79$  and 149.36 ppm) compared with **1a–g** [19].

By addition of a solution of  $ZnCl_2$  to a solution of  $H_2L$  in methanol, at  $pH \geq 5$ , a white precipitate of **6** [ $K_2(ZnLCl_2)$ ] was formed (figure 3). The IR spectrum of **6** showed stretches for NH, C=N and N–O at 3245, 1647 and 931, respectively, while the OH absorption vanished. The EI mass spectrum showed the molecular ion peak at  $m/z$  406 ( $M - 78$ ) and elemental analysis is consistent for  $K_2(ZnLCl_2)$ . The proton spectrum has a singlet at  $\delta 13.12$  ppm for NH and a multiplet for pyridine protons at 6.98–8.85 ppm. In the  $^{13}C$  NMR spectrum of **6**, resonance of dioxime groups was

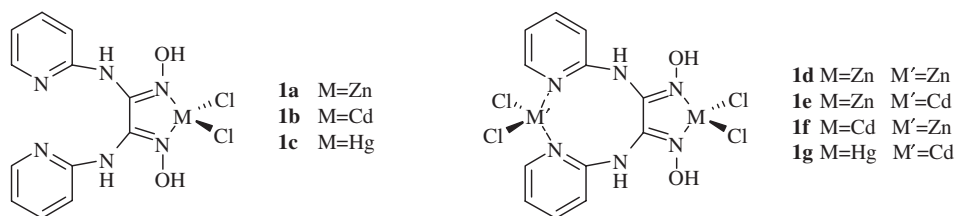


Figure 1. Suggested structure of the tetrahedral  $N,N$ -coordination ( $MM'H_2LCl_4$ ) complexes ( $M, M' = Zn(II), Cd(II), Hg(II)$ ).

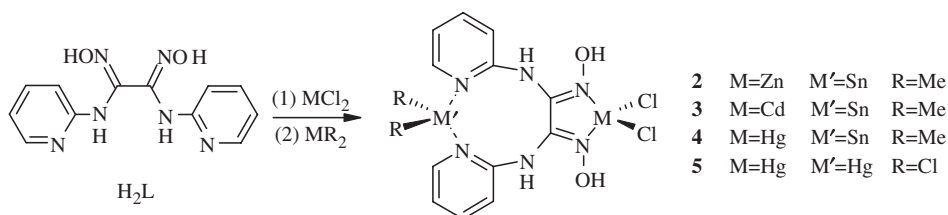


Figure 2. Suggested structures for  $N,N$ -coordinated complexes ( $MM'H_2LCl_2R_2$ ).

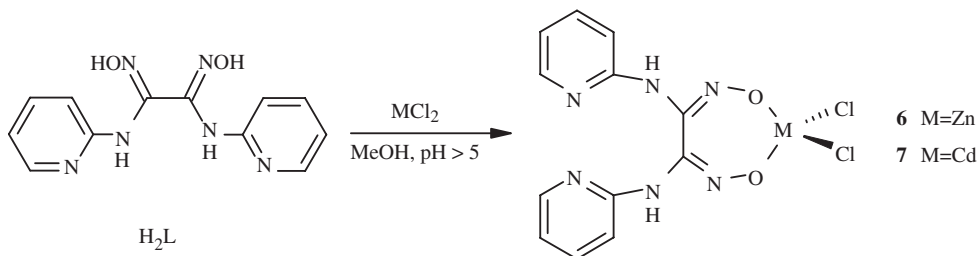


Figure 3. Suggested structure for  $K_2[MLCl_2]$  complexes.

observed at 151.65. The aromatic pyridine carbons appeared at 138.75–111.98 ppm. Coordination complexes in which the H<sub>2</sub>L forms a seven-member chelate ring by coordination to a metal through the O,O atoms, figure 3, have been reported previously [20]. Compound **7** was obtained in a similar condition. By doing these reactions at pH ≤ 3 the *N,N*-coordinated compounds **1a–c** are obtained.

In order to synthesize homo and hetero dinuclear O,O-coordinated complexes of the type K<sub>2</sub>[ZnMLCl<sub>4</sub>] M = Zn(II), Cd(II), and Hg(II) reactions of **6** were carried out with solutions of chloride salts of Zn(II), Cd(II) and Hg(II), **8–10** (figure 4). In the case of **8**, the EI mass spectrum, showed the molecular ion at *m/z* 542 [M – 78] and elemental analysis is consistent for K<sub>2</sub>[ZnMLCl<sub>4</sub>]. In the IR spectrum of **8**, the NH, C=N and N–O stretches are at 3245, 1643 and 948 cm<sup>-1</sup>, respectively, and lack OH absorption. In the <sup>1</sup>H NMR spectrum of **8**, NH was observed at δ = 8.61 ppm as a singlet and disappeared with D<sub>2</sub>O exchange. The pyridyl protons are at δ = 7.01–7.94 ppm, as a multiplet. The results show that, H<sub>2</sub>L acts as a bidentate bridging ligand toward metal ions. Therefore, we assume that one metal ion coordinates to the *vic*-dioxime groups as an O,O-coordinating complex of H<sub>2</sub>L and the other coordinates to N atoms of pyridyl aromatic rings (figure 4).

Compound **11** was prepared by refluxing a solution of **6** and Me<sub>2</sub>SnCl<sub>2</sub> in methanol (figure 4). The EI mass spectrum, showed the molecular ion at *m/z* 555 and elemental analysis is consistent for [Me<sub>2</sub>SnLZnCl<sub>2</sub>]. In the IR spectrum of **11** the N–H, CH<sub>3</sub>, C=N and N–O stretching vibrations were at 3219, 2920–2960, 1645 and 999, respectively. In the <sup>1</sup>H NMR of **11** the NH was observed at 8.62 ppm as a singlet and disappeared with D<sub>2</sub>O exchange. The pyridyl protons appeared at δ = 6.88–8.02 ppm, as a multiplet.

Recently we proposed different models for coordination of H<sub>2</sub>L to Zn(II) in mono and dinuclear complexes [21]. *Ab initio* and density functional calculations were used to study the coordination and thermodynamic properties of mono- and dinuclear complexes of zinc(II) with H<sub>2</sub>L at HF/3-21G\* and B3LYP/6-311 + G(2d,p)//HF/3-21G\* computational levels.

For complexation of ZnCl<sub>2</sub> with H<sub>2</sub>L four mononuclear as well as two dinuclear model structures were considered.

In H<sub>2</sub>L because of resonance between amines N lone pairs with the C=N bond of oximic functions nitrogens show diminished tendency for coordination to Zn atom. Theoretical calculation predicts less tendency of amines (N21, N23) for coordination to Zn(II), oximic (N27, N28) and pyridines (N6, N19) atom a comparable tendency for

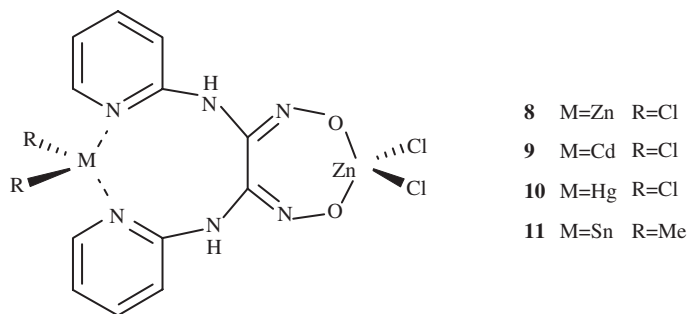


Figure 4. Suggested structure for O,O-coordinated K<sub>2</sub>(ZnMLCl<sub>4</sub>), M = Zn, Cd, Hg, and (Me<sub>2</sub>SnLZnCl<sub>2</sub>) complexes.

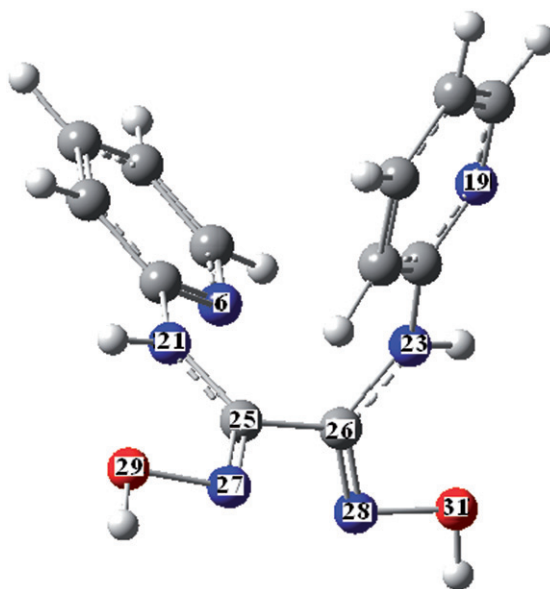


Figure 5. Structure of  $H_2L$  and  $L^{2-}$  optimized at HF/3-21G\* [21].

coordination to Zn(II) and unusual O,O-coordination (through  $L^{2-}$ ) gives the most stable model for mono nuclear complexes [21].

On the other hand, for dinuclear complexes theoretical calculations are indicating that coordination through O,O- and pyridines N atoms for  $L^{2-}$  and oximic and pyridines N atoms for  $H_2L$  were preferred. Experimental results of present work are confirming the predictions of our previous theoretical studies.

### 3. Experimental

#### 3.1. Material and measurements

All chemical reagents were obtained from Merck or Fluka and used without further purification. Melting points were measured on an Electrothermal 9200 apparatus and are uncorrected. Elemental analyses for C, H and N were performed using a Heraeus CHN-O rapid analyzer. Mass spectra were recorded on a Shimadzu 5050 QD spectrometer.  $^1H$  and  $^{13}C$  NMR spectra were recorded with a Bruker DRX-500 AVANCE in  $DMSO-d_6$  as solvent. The IR spectra were recorded on a Shimadzu IR-460 spectrometer.

**3.1.1. Synthesis of  $[ZnH_2LCl_2SnMe_2]Cl_2$  (2).** To a stirred solution of **1a** [19] (0.405 g, 1 mmol) in 35 mL methanol, a solution of  $Me_2SnCl_2$  (0.219 g, 1 mmol) in 15 mL methanol was added dropwise at room temperature. The mixture was refluxed for 2 h and the solvent was removed by evaporation. The brown precipitate was washed with 2-propanol, chloroform, diethyl ether and recrystallized from acetonitrile/water (2/1). Yield: 0.41 g (74.32%); m.p. 218°C. Elemental analysis, calculated for

$C_{14}H_{18}N_6O_2Cl_4SnZn$ : C, 26.75; H, 2.87; N, 13.38. Found: C, 26.68; H, 2.80; N, 13.26. EI-MS:  $m/z$  557  $[M - 71]^+$ . IR (KBr):  $\nu_{max}$  ( $cm^{-1}$ ): 3091–3205 ( $\nu$  OH), 3326 ( $\nu$  NH), 1643 ( $\nu$  C=N), 1620, 1500 ( $\nu$  C=C), 1257 ( $\nu$  C–N), 988 ( $\nu$  N–O), 769.  $^1H$  NMR ppm: 13.38 (s, 2H, OH), 12.41 (s, 2H, NH), 7.30–8.66 (m, 8H,  $ArH_{Py}$ ), 2.57 (s, 6H,  $CH_3$ ).  $^{13}C$  NMR ppm: 150.79, 149.36, 146.82, 146.67, 138.44, 137.19, 136.66, 129.35, 116.49, 115.64, 111.29, 111.11, 40.41.

**3.1.2. Synthesis of  $[MH_2LCl_2SnMe_2](M=Cd, Hg)Cl_2$  (3,4).** To a stirred solution of  $H_2L$  (0.272 g, 1 mmol) in 30 mL methanol, a solution containing 1 mmol of  $MCl_2$  (0.201 g  $CdCl_2$ , 0.272 g  $HgCl_2$ ) in 10 mL methanol was added dropwise at 50°C. The mixture was refluxed for 2 h then a solution of  $Me_2SnCl_2$  (0.219 g, 1 mmol) in 15 mL methanol was added dropwise at room temperature. The mixture was refluxed for 2 h again then solvent was removed by evaporation. The brown precipitate was washed several times with chloroform, diethyl ether and recrystallized from acetonitrile/water (2/1).

Compound **3**: Yield: 0.42 g (69.50%); m.p. 199.5°C. Elemental analysis, calculated for  $C_{14}H_{18}N_6O_2CdCl_4Sn$ : C, 24.88; H, 2.68; N, 12.44. Found: C, 24.71; H, 2.61; N, 12.45. EI-MS:  $m/z$  604  $[M - 71]^+$ . IR (KBr):  $\nu_{max}$  ( $cm^{-1}$ ): 3085–3190 ( $\nu$  OH), 3132 ( $\nu$  NH), 1664 ( $\nu$  C=N), 1650, 1523 ( $\nu$  C=C), 1242 ( $\nu$  C–N), 995 ( $\nu$  N–O).  $^1H$  NMR ppm: 13.51 (s, 2H, OH), 12.46 (s, 2H, NH), 7.30–8.66 (m, 8H,  $ArH_{Py}$ ), 2.53 (s, 6H,  $CH_3$ ).  $^{13}C$  NMR ppm: 150.43, 149.24, 147.02, 146.64, 138.20, 136.80, 133.34, 129.34, 116.59, 115.99, 111.09, 40.09.

Compound **4**: Yield: 0.53 g (76.60%); m.p. 202.5°C. Elemental analysis, calculated for  $C_{14}H_{18}N_6O_2HgSnCl_4$ : C, 22.02; H, 2.36; N, 11.01. Found: C, 21.96; H, 2.35; N, 11.00. EI-MS:  $m/z$  692  $[M - 71]^+$ . IR (KBr):  $\nu_{max}$  ( $cm^{-1}$ ): 3115–3211 ( $\nu$  OH), 3238 ( $\nu$  NH), 1649 ( $\nu$  C=N), 1631, 1523 ( $\nu$  C=C), 1264 ( $\nu$  C–N), 945 ( $\nu$  N–O).  $^1H$  NMR ppm: 13.49 (s, 2H, OH), 12.45 (s, 2H, NH), 7.31–8.66 (m, 8H,  $ArH_{Py}$ ), 2.53 (s, 6H,  $CH_3$ ).  $^{13}C$  NMR ppm: 150.47, 149.26, 146.97, 146.82, 138.24, 136.85, 136.74, 133.41, 129.34, 116.55, 115.92, 111.08, 40.09.

**3.1.3. Synthesis of  $[Hg_2H_2LCl_4]$  (5).** A solution of  $HgCl_2$  (0.272 g, 1 mmol) in 10 mL methanol was added dropwise to a stirred solution of  $H_2L$  (0.272 g, 1 mmol) in 35 mL pyridine at room temperature. The mixture was refluxed for 2 h then a solution of  $HgCl_2$  (0.272 g, 1 mmol) in 15 mL methanol was added slowly to this solution. The mixture was refluxed for 2 h again before solvent removal by evaporation. The yellow precipitate was washed with diethyl ether and recrystallized from acetonitrile/pyridine (2/1). Yield: 0.506 g (62.3%); m.p. 207°C. Elemental analysis, calculated for  $C_{12}H_{12}N_6O_2Cl_4Hg_2$ : C, 17.67; H, 1.47; N, 10.31. Found: C, 17.64; H, 1.45; N, 10.29. EI-MS:  $m/z$  815  $[M - 1]^+$ . IR (KBr):  $\nu_{max}$  ( $cm^{-1}$ ): 3312–3393 ( $\nu$  OH), 3226 ( $\nu$  NH), 1650 ( $\nu$  C=N), 1698 ( $\nu$  C=C), 1291 ( $\nu$  C–N), 981 ( $\nu$  N–O).  $^1H$  NMR ppm: 12.07 (s, 2H, OH), 11.19 (s, 2H, NH), 6.43–7.89 (m, 8H,  $ArH_{Py}$ ).  $^{13}C$  NMR ppm: 157.92, 156.86, 150.99, 149.85, 142.54, 140.10, 134.34, 127.42, 116.45, 116.14, 109.17, 108.23.

**3.1.4. Synthesis of  $K_2[ZnLCl_2]$  (6).** A solution of  $ZnCl_2$  (0.137 g, 1 mmol) in 10 mL methanol was added dropwise to a stirred solution of  $H_2L$  (0.272 g, 1 mmol) in 30 mL methanol at 60°C. The pH dropped to about 3 and rose to 4.8–5 by addition of KOH (0.056 g, 1 mmol) in 10 mL methanol. The mixture was refluxed for 2 h and the solvent was removed by evaporation. The orange precipitate was washed several times with acetonitrile and diethyl ether and recrystallized from  $H_2O$ . Yield: 0.276 g (68%); m.p. 204.5°C. Elemental analysis, calculated for  $C_{12}H_{10}N_6O_2Cl_2K_2Zn$ : C, 29.75; H, 2.07; N, 17.36. Found: C, 29.70; H, 2.00; N, 17.32. EI-MS:  $m/z$  406  $[M - 78]^+$ . IR (KBr):  $\nu_{max}$  ( $cm^{-1}$ ): 3245 ( $\nu$  NH), 1647 ( $\nu$  C=N), 1604, 1502 ( $\nu$  C=C), 1294, 1137 ( $\nu$  C-N), 931 ( $\nu$  N-O).  $^1H$  NMR ppm: 13.12 (s, 2H, NH), 6.98–8.85 (m, 8H,  $ArH_{Py}$ ).  $^{13}C$  NMR ppm: 151.65, 138.75, 131.15, 130.67, 117.61, 111.98.

**3.1.5. Synthesis of  $K_2[CdLCl_2]$  (7).** A solution of  $CdCl_2$  (0.201 g, 1 mmol) in 10 mL methanol was added dropwise to a stirred solution of  $H_2L$  (0.272 g, 1 mmol) in 35 mL pyridine at room temperature. The mixture was refluxed for 2 h and the solvent was removed by evaporation. The orange precipitate was washed several times with acetonitrile, pyridine and diethyl ether and recrystallized from 1-propanol/diethyl ether/chloroform (1/1/1). Yield: 0.337 g (78.8%); m.p. 201.5°C. Elemental Analysis, Calcd for  $C_{12}H_{10}N_6O_2Cl_2K_2Cd$ : C, 27.12; H, 1.88; N, 15.82. Found: C, 27.08; H, 1.80; N, 15.78. EI-MS:  $m/z$  453  $[M - 78]^+$ . IR (KBr):  $\nu_{max}$  ( $cm^{-1}$ ): 3234 ( $\nu$  NH), 1651 ( $\nu$  C=N), 1612, 1511 ( $\nu$  C=C), 1328 ( $\nu$  C-N), 1139 ( $\nu$  C-N), 933 ( $\nu$  N-O).  $^1H$  NMR ppm: 12.60 (s, 2H, NH), 7.37–8.58 (m, 8H,  $ArH_{Py}$ ).  $^{13}C$  NMR ppm: 149.58, 141.53, 136.47, 129.41, 124.04, 117.53.

**3.1.6. Synthesis of  $K_2[Zn_2LCl_4]$  (8).** (a) A solution of  $ZnCl_2$  (0.137 g, 1 mmol) in 10 mL methanol was added dropwise to a stirred solution of  $H_2L$  (0.272 g, 1 mmol) in 30 mL methanol at room temperature. The pH dropped to about 3 and rose to 4.8–5 by addition of KOH (0.056 g, 1 mmol) in 10 mL methanol. Then a solution of  $ZnCl_2$  (0.137 g, 1 mmol) in 15 mL methanol was added dropwise to the reaction mixture at room temperature. The mixture was refluxed for 2 h and the solvent was evaporated to dryness under reduced pressure. The orange-yellow precipitate was washed several times with acetonitrile, 1-propanol, ethylacetate and diethyl ether and recrystallized from acetonitrile/water (2/1). Yield: 0.424 g (78.2%); m.p. 248°C. Elemental analysis, calculated for  $C_{12}H_{10}N_6O_2Cl_4K_2Zn_2$ : C, 23.22; H, 1.61; N, 13.54. Found: C, 23.19; H, 1.58; N, 13.49. EI-MS:  $m/z$  542  $[M - 78]^+$ . IR (KBr):  $\nu_{max}$  ( $cm^{-1}$ ): 3245 ( $\nu$  NH), 1643 ( $\nu$  C=N), 1604, 1542 ( $\nu$  C=C), 1338 ( $\nu$  C-N), 948 ( $\nu$  N-O).  $^1H$  NMR ppm: 8.61 (s, 2H, NH), 7.01–7.94 (m, 8H,  $ArHPy$ ). (b) To a stirred solution of **6** (0.405 g, 1 mmol) in 35 mL methanol, a solution of  $ZnCl_2$  (0.137 g, 1 mmol) in 15 mL methanol was added dropwise at room temperature. The pH was kept about 4.85–5 by addition of KOH (0.056 g, 1 mmol) in 10 mL methanol. The mixture was refluxed for another 2 h then solvent was evaporated to dryness under reduced pressure.

**3.1.7. Synthesis of  $K_2[ZnMLCl_4]$  (M=Cd, Hg) (9,10).** The procedure 2.8 (b) was carried out but with 1 mmol of  $MCl_2$  (0.201 g  $CdCl_2$ , or 0.272 g  $HgCl_2$ ). A white

precipitate was obtained, washed with 1-propanol and diethyl ether and recrystallized from acetonitrile/pyridine (1/1).

Compound **9**: Yield: 0.425 g (76.7%); m.p. 308°C Elemental analysis, calculated for  $C_{12}H_{10}N_6O_2Cl_4CdK_2Zn$ : C, 21.55; H, 1.50; N, 12.57. Found: C, 21.50; H, 1.45; N, 12.53. EI-MS:  $m/z$  590  $[M - 78]^+$ , 589  $[M - 79]^+$ . IR (KBr):  $\nu_{max}$  ( $cm^{-1}$ ): 3253 ( $\nu$  NH), 1633 ( $\nu$  C=N), 1612, 1487 ( $\nu$  C=C), 1220 ( $\nu$  C-N), 1012 ( $\nu$  N-O).  $^1H$  NMR ppm: 8.58 (s, 2H, NH), 7.39–7.81 (m, 8H,  $ArH_{Py}$ ).

Compound **10**: Yield: 0.497 g (73.4%); m.p. 238°C Elemental analysis, calculated for  $C_{12}H_{10}N_6O_2Cl_4HgK_2Zn$ : C, 19.05; H, 1.32; N, 11.11. Found: C, 18.98; H, 1.27; N, 11.07. EI-MS:  $m/z$  678  $[M - 78]^+$ , 677  $[M - 79]^+$ . IR (KBr):  $\nu_{max}$  ( $cm^{-1}$ ): 3227 ( $\nu$  NH), 1647 ( $\nu$  C=N), 1604, 1466 ( $\nu$  C=C), 1226 ( $\nu$  C-N), 1010 ( $\nu$  N-O).  $^1H$  NMR ppm: 8.63 (s, 2H, NH), 6.79–7.97 (m, 8H,  $ArH_{Py}$ ).

**3.1.8. Synthesis of  $[ZnLCl_2SnMe_2]$  (11).** According to procedure 2.8 (b) with  $Me_2SnCl_2$  (0.219 g, 1 mmol) an orange product precipitated. The product was washed with acetonitrile, 2-propanol, diethyl ether and chloroform and then recrystallized from water. Yield: 0.423 g (76.21%); m.p. 232°C. Elemental analysis, calculated for  $C_{14}H_{16}N_6O_2Cl_2SnZn$ : C, 30.27; H, 1.88; N, 15.14. Found: C, 30.24; H, 1.86; N, 15.15. EI-MS:  $m/z$  555  $[M]^+$ . IR (KBr):  $\nu_{max}$  ( $cm^{-1}$ ): 3335 ( $\nu$  NH), 2920–2960 ( $\nu$   $CH_3$ ), 1645 ( $\nu$  C=N), 1596, 1541 ( $\nu$  C=C), 1224 ( $\nu$  C-N), 999 ( $\nu$  N-O).  $^1H$  NMR ppm: 8.62 (s, 2H, NH), 6.88–8.02 (m, 8H,  $ArH_{Py}$ ), 2.53 (s, 6H,  $CH_3$ ).

## References

- [1] C. Grandmann, V. Mini, J.M. Dean, H.D. Frommheld. *Liebigs. Ann. Chem.*, **687**, 191 (1965).
- [2] J.J. Christensen, J.J. Eatough, R.M. Izatt. *Chem. Rev.*, **74**, 351 (1974).
- [3] J.R. Dilworth, S.J. Parrott. *Chem. Soc. Rev.*, **27**, 43 (1998).
- [4] M.D. Coburn, J. Heterocyclic. *Chem.*, **5**, 83 (1968).
- [5] A. Kakanejadifard, M. Farnia, G. Najafi. *Iran. J. Chem. & Chem. Eng.*, **23**, 118 (2004).
- [6] A. Chakravorty. *Coord. Chem. Rev.*, **13**, 1 (1974).
- [7] A. Bilgin, B. Ertem, F. Dinc-Agin, Y. Gok, S. Karslioglu. *Polyhedron*, **25**, 3165 (2006).
- [8] A. Kakanejadifard, E. Niknam, A. Zabardasti. *J. Coord. Chem.*, **60**, 677 (2007).
- [9] S. Farhadi, A. Kakanejadifard, N. Dorosti. *Polish J. Chem.*, **79**, 1829 (2005).
- [10] B. Ranjbar, S. Afshar, A. Kakanejadifard, K. Khajeh, H. Naderi-Manesh, L. Hassani, N. Alizadeh. *Asian. J. Biochem.*, **1**, 153 (2006).
- [11] G.N. Schrauzer, J. Kohnle. *Chem. Ber.*, **97**, 3056 (1964).
- [12] A.R. Ghiasvand, S. Shadabi, A. Kakanejadifard, A. Khajehkolaki. *Bull. Korean. Chem. Soc.*, **26**, 781 (2005).
- [13] A. Yari, S. Azizi, A. Kakanejadifard. *Sensor & Actuators B.*, **119**, 167 (2006).
- [14] M.E.B. Jones, D.A. Thornton, R.F. Webb. *Makromol. Chem.*, **49**, 62 (1961).
- [15] M.J. Prushan, A.W. Addison, R.J. Butcher. *Inorg. Chim. Acta*, **992**, 300 (2000).
- [16] J.P. Leonard, D.P. Novotnil, R.D. Neirickx. *J. Nucl. Med.*, **27**, 1819 (1986).
- [17] M.A. Green. *Adv. Met. Med.*, **1**, 75 (1993).
- [18] E.K. John, A.J. Bott, M.A. Green. *J. Pharm. Sci.*, **83**, 587 (1994).
- [19] A. Kakanejadifard, E. Niknam. *Polish J. Chem.*, **80**, 1645 (2006).
- [20] M.S. Singh, A.K. Singh. *Tetrahedron Lett.*, **46**, 315 (2005).
- [21] A. Zabardasti, A. Kakanejadifard, M. Salehnassaj, submitted. *Bull. Chem. Soc(Japan)* (2007).