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Synthesis and Characterization of Cd(II), Zn(II) and Hg(II) Chloride Adducts of (2Z,3Z)-1,4,7-Trithiononane-2,3-dionedioxime

ALI KAKANEJADIFARD*, ABEDIEN ZABARDASTI, MOTALEB GHASEMIAN and
HOSSEIN TOOSI-JAMALI
Department of Chemistry, Faculty of Science, Lorestan University
Falakalaflak Street, Khorramabad, Iran
Tel/Fax: (98)(661)2200185
E-mail: kakanejadi.a@lu.ac.ir, alikakanejadifard@yahoo.com

A New *vic*-dioxime, (2Z,3Z)-1,4,7-trithiononane-2,3-dionedioxime (H_2L) was prepared from reaction of 2-[2-mercaptoethyl)thio]ethanethiol with dichloroglyoxime. Mononuclear complexes of H_2L with Zn(II), Hg(II) and Cd(II) were also prepared and their structures were determined by means of NMR, IR and mass spectroscopy. The Hg(II), Cd(II) and Zn(II) form 1:1 tetrahedral complexes with a N,N-chelation.

Key Words: *vic*-Dioxime, Zn(II), Cd(II), Hg(II), 1,4,7-Trithionane-2,3-dionedioxime, N,N-Chelation.

INTRODUCTION

Diaminoglyoxime and dithioglyoximes as well as their metal complexes are of current interest due to their rich physicochemical[1-3], medical[4], bioorganic systems[5], catalysis, electrochemical and electrooptical sensors properties[6-14]. The coordination chemistry of multidentate thiamacrocycle and bidentate *vic*-dioximes has been studied[15,16]. In this work, we report the synthesis and characterization of smallest 9-membered trithiamacrocycle (2Z,3Z)-1,4,7-trithiononane-2,3-dionedioxime (H_2L) with a *vic*-dioxime unit and its complexes with Hg(II), Cd(II) and Zn(II) metal ions.

EXPERIMENTAL

All chemical reagents were obtained from Merck and were 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 Shimadzu 500 QD spectrometers. ^1H and ^{13}C NMR spectra were recorded with a Bruker DRX-500 Avance, DMSO-d_6 was used as solvent. IR spectra were recorded on a Shimadzu 4300 spectrometer.

Synthesis of (2Z,3Z)-1,4,7-trithiononane-2,3-dionedioxime (H_2L): A solution of sodium salt of 2-[2-mercapto ethyl)thio]ethanethiol was prepared by portionwise addition of the latter (1.30 mL, 10 mmol) to NaOEt solution obtained by dissolving sodium metal (0.46 g, 20 mmol) in absolute ethanol (70 mL). This solution was added dropwise over 5 h to a solution of dicholoroglyoxime (1.57 g, 10 mmol) in absolute ethanol (70 mL) at room temperature. The solution was stirred at room temperature for 24 h and then the yellow precipitate was filtered. The filtrate solution was concentrated to produce an oily yellow solution. Then purred in to heated THF and the white precipitates were collected. Recrystallization in MeCN-THF (2:1). Yield: 0.136 g, (57 %), m.p. 210-211 ºC. IR (KBr, ν_{max} cm^{-1}): 3400-3200 (O-H), 2970-2827 (C-H), 1570 (C=N), 987 (N-O) and 869-692 (C–S). ^1H NMR ppm: 12.09 (s, 2H, C=N–OH, exchangeable with D_2O), 3.05 (t, 4H, *J* = 7.25), 2.80 (t, 4H, *J* = 7.25). ^{13}C NMR ppm: 145.65 (C=N-OH), 31.86 and 31.10. The EI-MS, m/z: 238 (m^+), 220 (m-18).

Preparation of [(H_2L)MCl_2] complexes (M= Hg(II), Cd(II), Zn(II)): A solution of $MCl_2{\cdot}xH_2O$ (1 mmol in 25 mL MeOH) was added dropwise to a solution of H_2L (0.238 g, 1 mmol) in 25 mL MeOH at the room temperature. The pH dropped to about 4 and rose to 5-5.5 by addition of KOH (0.056 g, 1 mmol) in 10 mL MeOH. The mixture was refluxed for 2 h. The precipitate was filtered and washed with H_2O, Et_2O and then dried.

[(H_2L)$HgCl_2$] Complex: This yellow-white complex was prepared by the procedure described above, starting from $HgCl_2{\cdot}H_2O$ (0.273 g, 1 mmol) and H_2L (0.238 g, 1 mmol). Yield: 0.212 (54 %), m.p. > 177 ºC. IR (KBr, ν_{max}, cm^{-1}): 3350-3313 (O-H) 2943, 2904 (CH_2), 1580 (C=N), 976 (N-O). ^1H NMR ppm: 8.55 (s, 2H, C=N-OH, exchangeable with D_2O), 3.09 (t, 4H, *J* = 5.76 Hz), 2.85 (t, 4H, *J* = 5.76 Hz). ^{13}C NMR ppm: 124.60 (C=N-OH), 37.18 and 29.06. MS; m/z = 507 (m^+). Elemental analysis, calculated for $C_6H_{10}N_2O_2S_3Cl_2Hg$: C, 14.21; H, 1.97; N, 5.53. Found: C, 14.18; H, 2.01; N, 5.56.

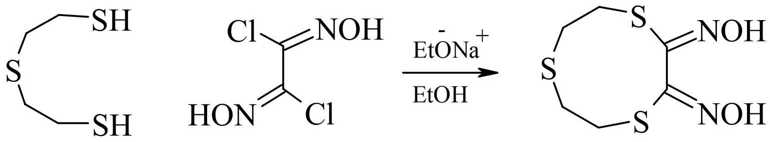
[(H_2L)$CdCl_2$] Complex: This yellow-white complex was prepared by the procedure described above, starting from $CdCl_2{\cdot}H_2O$ (0.201 g, 1 mmol) and H_2L (0.238 g, 1 mmol). Yield: 0.232 g (51 %) m.p. >196ºC. IR (KBr, ν_{max}, cm^{-1}): 3330-3229 (O-H) 2970, 2914 (CH_2), 1569 (C=N), 987 (N-O). ^1H NMR ppm: 12.08 (s, 2H, C=N-OH, exchangeable with D_2O), 3.04 (t, 4H, *J* = 6.61 Hz), 2.78 (t, 4H, *J* = 6.61 Hz). ^{13}C NMR ppm: 141.01 (C=N-OH), 37.18 and 29.06. MS; m/z = 422 (m+4), 420 (m+2), 418 (m^+). Elemental analysis, calculated for $C_6H_{10}N_2O_2S_3Cl_2Cd$: C, 17.20; H, 2.39; N, 6.70. Found: C, 17.17; H, 2.43; N, 6.68.

[(H_2L)$ZnCl_2$] Complex: This brown complex was prepared by the procedure described above starting from $ZnCl_2$ (0.137 g, 1 mmol) and H_2L (0.238 g, 1 mmol). Yield: 0.192 g (45 %), m.p. >167 ºC. IR (KBr, ν_{max}, cm^{-1}):

3209-3147 (O-H), 2970, 2808 (CH_2), 1589 (C=N), 995 (N-O). ^1H NMR ppm: 12.79 (s, 2H, C=N-OH, exchangeable with D_2O), 3.35 (t, 4H, J = 6.23 Hz), 2.49 (t, 4H, J = 6.23 Hz) MS; m/z =374 (m+2), 371 (m+), 370 (m-1). Elemental analysis, calculated for $C_6H_{10}N_2O_2S_3Cl_2Zn$: C, 19.38; H, 2.70; N, 7.54. Found: C, 19.41; H, 2.69; N, 7.55.

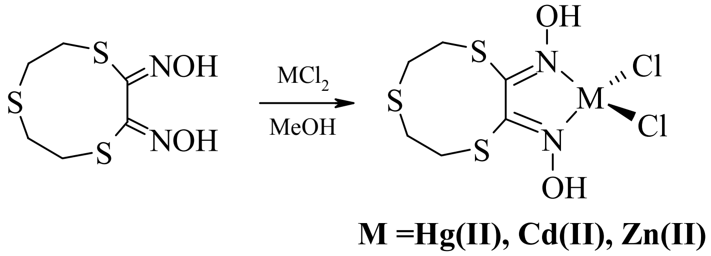
RESULTS AND DISCUSSION

The compound H_2L was prepared from the reaction of 2-[2-mercaptoethyl)thio]ethanethiol with dichloroglyoxime in MeOH. In the IR spectrum, disappearance of the S-H stretching band, along with the appearance of new absorptions at 3400-3200 (O-H), 2970-2827 (C-H), 1569 (C=N), 987 (N-O) and 869-692 cm^{-1} (C-S), is in agreement with the structure of H_2L (**Scheme-I**). ^1H NMR spectrum of H_2L exhibits two triplets for CH_2 groups at 3.05 and 2.80 and a singlet at 12.09 ppm. The chemical shifts for the C=N are found at 145.65 ppm in ^{13}C NMR spectrum. The chemical shifts for CH_2 groups are found at 31.86 ppm and 31.10 ppm. The mass spectrum of H_2L exhibits a molecular ion peak at m/z = 238.



Scheme-I: Preparation and structural formula of the H_2L

The reaction of H_2L with chloride salts of Hg(II), Cd(II) and Zn(II) in pH > 5.5, gives complexes of molar ratio 1:1 of metal to ligand (**Scheme-II**). The IR spectra of the complexes are close to those of H_2L. In the ^1H NMR spectrum of $(H_2L)HgCl_2$, the deuterium exchangeable OH protons were observed at 8.55 ppm as a singlet and two triplets for CH_2 protons at 3.09, 2.85 ppm. ^{13}C NMR ppm: 124.60 (C=N-OH), 37.18 and 29.06. The NMR data for Cd(II) and Zn(II) complexes are similar to those found for the Hg(II). The structure of these complexes is also confirmed by mass spectroscopy, which give molecular ion peaks (M^+) for $[(H_2L)HgCl_2]$, $[(H_2L)CdCl_2]$ and $[(H_2L)ZnCl_2]$ complexes at m/z 506, 418 and 371, respectively. This data revealed that, for the case Hg(II), Cd(II) and Zn(II) complexes, the coordination is more usual in tetrahedral (Z,Z)-complexes. The ligand forms a five-member chelate ring by coordination to metal through two N atoms.



Scheme-II: Proposed structure for the tetrahedral complex of the $(H_2L)MCl_2$

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