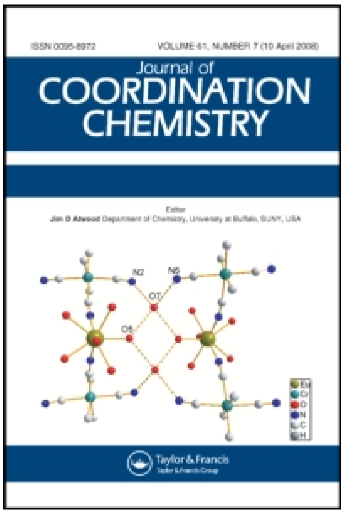

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Synthesis and complexation of 1,4,7-oxadithiononane-5,6-dionedioxime

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Synthesis and complexation of 1,4,7-oxadithiononane-5,6-dionedioxime

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A new *vic*-dioxime 1,4,7-oxadithiononane-5,6-dionedioxime (**H_2L**) was prepared from reaction of 2,2-oxydiethanthiol with dichloroglyoxime. Mononuclear complexes of **H_2L** with Ni(II), Co(II), Cu(II), Zn(II), and Cd(II) were also prepared and their structures were determined by means of ^{1}H NMR, ^{13}C NMR, IR, and mass spectroscopy. Ni(II), Co(II), and Cu(II) form square planar complexes of 1 : 2 molar ratio of metal to ligand through N,N-chelation, while Zn(II) and Cd(II) form 1 : 1 tetrahedral complexes with a N,O-chelation.

Keywords: vic-Dioxime; 1,4,7-Oxadithiononane-5,6-dionedioxime; Dichloroglyoxime; N,N-Chelation; N,O-Chelation

1. Introduction

Oxime ligands are used as analytical reagents [1, 2] and serve as models for biological systems [3–5] as well as catalysts in chemical processes [6, 7]. Dioxime ligands are also successful sequestering agents for transition metals and other ions [8]. *vic*-Dioximes and their complexes constitute an important class of compounds having versatile reactivity [6, 7]. Since the discovery of cobaloximes as model compounds for coenzyme B_{12} many advances have been made in structural and spectroscopic methodologies [9]. Hydrogen bridges stabilize the planar structure of *vic*-dioxime complexes. Moreover by removing the hydrogen bridge polymetallic complexes of various *vic*-dioximes have been synthesized [10–14]. Furthermore, *vic*-dioximes are easily modified by substitution with various groups. The reaction of amines or thiols with dichloroglyoxime or cyanogendi-N-oxide yielded various symmetrically substituted diaminoglyoxime or dithioglyoxime derivatives [15, 16]. In this study, the synthesis and characterization of a new (*Z*,*Z*)-dioxime ligand and its complexes with Cu(II), Ni(II), Co(II), Cd(II) and Zn(II) are described.

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2. Experimental

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. Mass spectra were recorded on a Shimadzu 5000 QD spectrometer. ^{1}H 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 4300 spectrometer. Elemental analyses for C, H and N were performed using a Heraeus CHN–C Rapid analyzer.

Preparation of (5*Z*,6*Z*)-1,4,7-oxadithiononane-5,6-dionedioxime (H_2L). A solution of the sodium salt of 2,2-oxydiethanthiol was prepared by portion-wise addition of the latter (1.24 mL, 10 mmol) to a NaOEt solution obtained by dissolving sodium metal (0.46 g, 20 mmol) in absolute EtOH (70 mL). This solution was added dropwise over 5 h to a solution of dichloroglyoxime (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 pale yellow precipitate was filtered. The precipitates were treated with water (40 mL) at 35°C to completely remove the NaCl formed. The *vic*-dioxime was filtered off and washed with EtOH, Et_2O and dried. Recrystallization in MeOH–THF (1 : 1) gave 1.488 g (67% yield) of the white product, m.p. 181°C. It is soluble in DMSO, acetone, and THF. ^{1}H NMR ppm: 12.02 (s, 2H, disappears upon deuterium exchange), 3.52 (t, 4H, $J = 5.24$), 2.92 (t, 4H, $J = 5.24$). ^{13}C NMR ppm: 145.55 (C=N–OH), 69.09 and 29.31 ppm. IR (KBr) cm^{-1}: 3200–3400 (O–H), 2975, 2995 (CH_2), 1585 (C=N), 1095 (C–O), 980 (N–O), and 880, 635 (C–S). The EI-MS, m/z: 222 (m$^+$), 204 (m − 18). Anal. Calcd for $C_6H_{10}N_2S_2O_3$: C, 32.43; H, 4.50; N, 12.61. Found: C, 32.39; H, 4.49; N, 12.58.

Preparation of [M(HL)$_2$] complexes (M = Ni, Co, Cu). A solution of $MCl_2 \cdot xH_2O$ (0.5 mmol) in methanol (25 mL) was added dropwise to a solution of $\mathbf{H_2L}$ (0.222 g, 1 mmol) in THF (50 mL) at room temperature. The color of the solution immediately changed and the pH dropped to about 3. The pH was raised to 5–5.5 by addition of KOH (0.056 g, 1 mmol) in methanol (10 mL). The mixture was refluxed for 4 h, and the precipitate was filtered and washed with H_2O, THF and Et_2O and dried.

[Ni(HL)$_2$] complex. This red complex was prepared by a general procedure that was described in the last part, starting from $NiCl_2 \cdot 6H_2O$ (0.12 g, 0.5 mmol) and $\mathbf{H_2L}$ (0.222 g, 1 mmol). This compound is slightly soluble in DMSO and DMF. Yield: 87%; m.p. >240°C. IR (KBr) cm^{-1}: $v = 2925$–2996 ($\upsilon_{\text{CH–aliph}}$), 1708 ($\upsilon_{\text{O–H}\cdots\text{O}}$), 1630 ($\upsilon_{\text{C=N}}$), 1105 ($\upsilon_{\text{C–O}}$), 887 ($\upsilon_{\text{N–O}}$); ^{1}H NMR ppm: 17.93 (s, O–H$\cdots$O, exchangeable with D_2O), 3.97 (t, CH_2–O), 2.97 (t, CH_2–S). MS; $m/z = 500$. Anal. Calcd for $C_{12}H_{18}N_4S_4O_6Ni$: C, 28.80; H, 3.60; N, 11.20. Found: C, 28.77; H, 3.64; N, 11.16.

[Co(HL)$_2$] complex. The dark brown complex was prepared following the same procedure as described above, starting from $CoCl_2 \cdot 6H_2O$ (0.12 g, 0.5 mmol) and $\mathbf{H_2L}$ (0.222 g, 1 mmol). This compound is also slightly soluble in DMSO and DMF. Yield: 70%. m.p. 230°C. IR (KBr) cm^{-1}: $v = 2927$ ($\upsilon_{\text{CH–aliph}}$), 1705 ($\upsilon_{\text{OH}\cdots\text{O}}$), 1630 ($\upsilon_{\text{C=N}}$), 1105 ($\upsilon_{C\text{–}O}$), 881 ($\upsilon_{N\text{–}O}$). ^{1}H NMR ppm: 13.6 (s, O–H $\cdots$ O exchangeable with D_2O), 3.60 (t, CH_2–O), 2.62 (t, CH_2–S). MS; $m/z = 501$. Anal. Calcd for $C_{12}H_{18}N_4S_4O_6Co$: C, 28.74; H, 3.59; N, 11.17. Found: C, 28.76; H, 3.62; N, 11.16.

[Cu(HL)$_2$] complex. This dark green complex was prepared by the same procedure mentioned above starting from $CuCl_2 \cdot 2H_2O$ (0.12 g, 0.5 mmol) and **H_2L** (0.222 g, 1 mmol). This compound is soluble in DMSO and DMF. Yield: 83% m.p. 247°C. IR (KBr): $v = 2884$–2985 ($\upsilon_{CH\text{–aliph}}$), 1703 ($\upsilon_{O\text{–}H \cdots O}$), 1631 ($\upsilon_{C=N}$), 1099 ($\upsilon_{C\text{–}O}$), 1196 ($\upsilon_{N\text{–}O}$). ^{1}H NMR ppm: 13.59 (s, O–H $\cdots$ O, disappeared upon deuterium exchange), 3.95–3.97 (t, CH_2–O, $J = 4.87$ Hz), 2.84–2.85 (t, CH_2–S, $J = 4.87$ Hz). ^{13}C NMR ppm: 124.62, 72.14, and 41.03. MS; $m/z = 523(m+18)$, $505(m^+)$. Anal. Calcd for $C_{12}H_{18}N_4S_4O_6Cu$: C, 28.51; H, 3.56; N, 11.09. Found: C, 28.48; H, 3.56; N, 11.08.

Preparation of [M(HL)Cl$_2$] complexes (M = Zn, Cd). A solution of $MCl_2 \cdot xH_2O$ (1 mmol) in MeOH (25 mL) was added dropwise to a solution of **H_2L** (0.222 g, 1 mmol) in THF (50 mL) at 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 4 h. The precipitate was filtered and washed with H_2O and Et_2O and then dried.

[Zn(HL)Cl$_2$] complex. This yellow complex was prepared by the procedure described above starting from $ZnCl_2$ (0.137 g, 1 mmol) and **H_2L** (0.222 g, 1 mmol). This compound is insoluble in DMSO, DMF, THF, ROH, H_2O and Et_2O. Yield 45%, m.p. >225°C. IR (KBr) cm^{-1}: $v = 3230$–3396 ($\upsilon_{O\text{–}H}$), 2926 ($\upsilon_{CH\text{–aliph}}$), 1579 ($\upsilon_{C=N}$), 1103 ($\upsilon_{C\text{–}O}$), 976 ($\upsilon_{N\text{–}O}$). MS; $m/z = 361(m+4)$, $358(m+1)$, $357(m^+)$. Anal. Calcd for $C_6H_9N_2S_2O_3ZnCl_2$: C, 20.16; H, 2.52; N, 7.84. Found: C, 20.10; H, 2.48; N, 7.85.

[Cd(HL)Cl$_2$] 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** (0.222 g, 1 mmol). This compound is also insoluble in DMSO, DMF, THF, ROH, H_2O and Et_2O. Yield 51%, m.p. >250°C. IR (KBr) cm^{-1}: $v = 3408$ ($\upsilon_{O\text{–}H}$) 2922 ($\upsilon_{CH\text{–aliph}}$), 1580 ($\upsilon_{C=N}$), 1105 ($\upsilon_{C\text{–}O}$), 975.9 ($\upsilon_{N\text{–}O}$). MS; $m/z = 405(m^+)$. Anal. Calcd for $C_6H_9N_2S_2O_3CdCl_2$: C, 17.77; H, 2.22; N, 6.91. Found: C, 17.70; H, 2.15; N, 6.95.

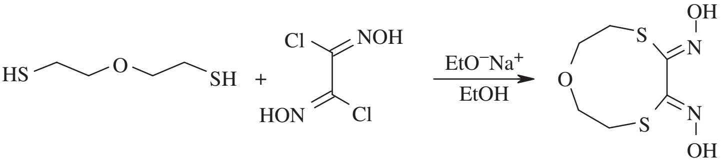
3. Results and discussion

The compound (5*Z*,6*Z*)-1,4,7-oxadithiononane-5,6-dionedioxime (**H_2L**) was prepared from the reaction of 2,2-oxydiethanthiol with a solution of dichloroglyoxime in absolute EtOH. The disappearance of the S–H stretching band, along with the appearance of new absorptions at 3200–3400 v(O–H), 2975–2995 v(C–H), 1585 v(C=N), 980 v(N–O) and 635–881 cm^{-1} v(C–S) is in agreement with the structure suggested in scheme 1. The ^{1}H NMR spectrum of **H_2L** exhibits two triplets at 3.51 (O–CH_2), 2.92 (S–CH_2) ppm and a singlet at 12.02 ppm (N–OH exchangeable with D_2O). In the ^{13}C NMR spectrum of **H_2L**, the chemical shifts of C=N appear at 145.55,

CH_2 groups at 69.09 (CH_2–O) and 29.30 ppm (CH_2–S). The mass spectrum of **H_2L** exhibits a molecular ion peak at $m/z = 222$.

The reaction of **H_2L** with chloride salts of Ni(II), Co(II) and Cu(II) gives complexes of mole ratio 1 : 2 of metal to ligand but for Zn(II) and Cd(II) 1 : 1 complex were obtained. A distinct decrease in the pH of the reaction solution during complex formation of Cu(II), Ni(II) and Co(II) with **H_2L** indicated deprotonation of the ligand with subsequent *N*,*N*′-chelation (figure 1). The IR spectra of the complexes are close to those of **H_2L**, except for the disappearance of the OH stretching frequencies for Cu(II), Ni(II) and Co(II) complexes.

Weak bands at ca 1703–1708 cm^{-1} indicated O–H ··· O hydrogen-bonded bridges while the C=N vibration appeared at lower wavenumbers [17–20], as expected for N,N′-chelated *vic*-dioxime complexes. In the ^1H NMR spectrum of $Cu(HL)_2$, the deuterium exchangeable O–H ··· O protons were observed at 13.59 ppm as a singlet and CH_2 protons at 2.84–2.85 (t, CH_2–S, $J = 4.87$ Hz) and 3.95–3.97 (t, CH_2–O, $J = 4.87$ Hz). The chemical shifts (^1H and ^{13}C NMR) were observed for Ni(II) while Co(II) complexes were similar to those found for the Cu(II) complex. For the Cd(II) and Zn(II) complexes, the IR spectrum showed that the OH stretching vibration of the oxime groups is still present at 3280 and 3396 cm^{-1}, respectively. In contrast to Ni(II), Co(II), and Cu(II) complexes, the characteristic band for the O–H ··· O stretches was not observed for Cd(II) and Zn(II) complexes. The structure of the complexes is also confirmed by mass spectroscopy, which gives a molecular ion peak (M^+) for $[Cd(HL)Cl_2]$ and $[Zn(HL)Cl_2]$ complexes at m/z 405 and 357, respectively. For Cd(II) and Zn(II) this type of coordination is more usual in (*E*,*Z*)-complexes. The ligand forms a six-membered chelate ring by coordination to metal through the N and O atoms as shown in figure 2.



Scheme 1. Preparation and structural formula of the *vic*-dioxime **H_2L**.

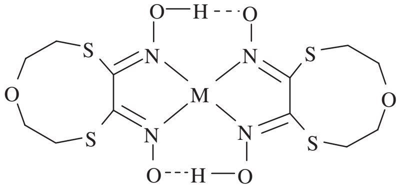


Figure 1. Suggested structure for the square planar complexes of $M(HL)_2$, M = Ni, Co, Cu.

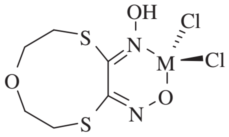


Figure 2. Suggested structure for the tetrahedral complex of $M(HL)Cl_2$, M = Zn, Cd.

Acknowledgments

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