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SYNTHESIS OF A NOVEL HETEROCYCLIC DIOXIME AND ITS MONONUCLEAR COMPLEXES WITH Ni(II), Co(II), Cu(II), Zn(II), Cd(II) and Hg(II)

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ABSTRACT

In this work, a novel heterocyclic dioxime (2,3-hydroximino-4-phenyl-6-phenlyazo-1-thia-4,5-diazacyclohexa-5-diene, H_2L) was synthesized by reacting dithizone with cyanogen di-N-oxide. H_2L forms mononuclear complexes $[(HL)_2M]$ with a metal-ligand ratio of 1:2 with M = Ni(II), Co(II) and Cu(II). Zn(II), Cd(II) and Hg(II) form with H_2L complexes $[(HL)Cl(H_2O)M]$ which have a metal-ligand ratio of 1:1 and contain a six-membered chelate ring. Structures of these compounds are proposed based on elemental analyses, U.V.-Visible, IR, ^1H NMR, mass spectra and magnetic susceptibility measurements.

INTRODUCTION

Metal complexes of vic-dioximes represent an important and interesting class of coordination compounds. vic-Dioximes have not only produced stable metal complexes of

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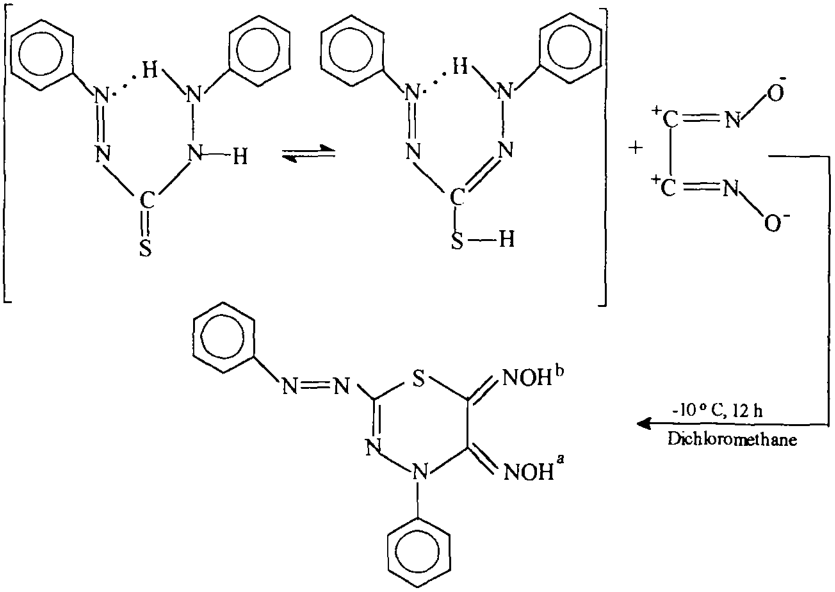
transition, inner-transition and actinide metal ions, but these ligands and their metal complexes have also played a significant role in the domains of stereochmestry, structure, isomerism, magnetism, spectroscopy, model systems of biochemical interest, cation exchange and ligand exchange chromatography, analytical chemistry, catalysis, stabilizers, polymers and pigments and dyes[1-17].

Although cyanogen di-N-oxide was first prepared[18] in 1911, its properties and reactions have been studied only in 1965 by Grundmann and his co-workers[19]. Besides having a tendency to give polymers, it reacts, like other nitrile oxides[20], with amines or 1,2-diamines to form substituted amidoximes, e.g. with o-phenylenediamine and ethylenediamine it gives 2,3-bishydroxyimino-1,2,3,4-tetrahyroquinoxaline and 2,3-bishydroxyimino-piperazine, respectively. The reaction was found to be a general one, treatment of various compounds which contain $-NH_2$, -SH and -OH with cyanogen di-N-oxide gave various vic-dioximes, respectively. The formation of polymers was avoided by keeping the reaction mixture cool and employing dilute solutions of the reactants. The yields, based on the anti-dichloroglyoxime used, were in the 40-50% range. The relative order of the reactivity of groups in the reaction with cyanogen di-N-oxide is $-NH_2$ >SH > OH[21,22].

We have previously reported on the synthetic chemistry of vic-dioximes[23-27]. Dithizone and its derivatives as well as various of its reactions were also reported[28-31]. However, published information related to dithizone and vic-dioximes does not seem to exist in the available literature references. For the present work, we synthesized a novel 6-membered thia-diazaheterocycle with a vic-dioxime unit incorporated (Fig. 1) end obtained mononuclear complexes with Ni(II), Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions.

RESULTS AND DISCUSSION

The ligand used for this study was 2,3-hydroximino-4-phenyl-6-phenlyazo-1-thia-4,5-diazacyclohexa-5-diene (H_2L). Its synthesis was accomplished in 95% yield by the reaction of cyanogen di-N-oxide and dithizone (H_2Dz) as shown in Fig. 1. The structure of H_2L was confirmed by a combination of elemental analyses, UV-Visible, ^1H NMR., mass and IR spectral data.



H_2L

Fig. 1. Synthesis of H_2L

^{1}H NMR, Mass and IR Spectra of H_2L

In the ^{1}H NMR spectra (in DMSO-d_6), two peaks are present for the OH protons of the oxime groups. These two deuterium-exchangeable singlets correspond to two non-equivalent OH protons that also indicate the anti-configuration of the OH groups relative to each other (Fig. 1). When the chemical shift values of the two OH groups in H_2L are compared, the one of them is observed at lower field ((δ_a = 12.53 ppm) and the other is observed at higher field (δ_b = 12.04 p.p.m.)[23,33,36]. Two multiplets at 7.91-7.14 ppm correspond to ten aromatic protons. The mass spectrum of H_2L, which shows a molecular ion at m/z 340.0767 (the theoretically calculated molecular weight: 340.00), confirms the proposed structure and rules out an undesired polymeric form (Fig. 2).

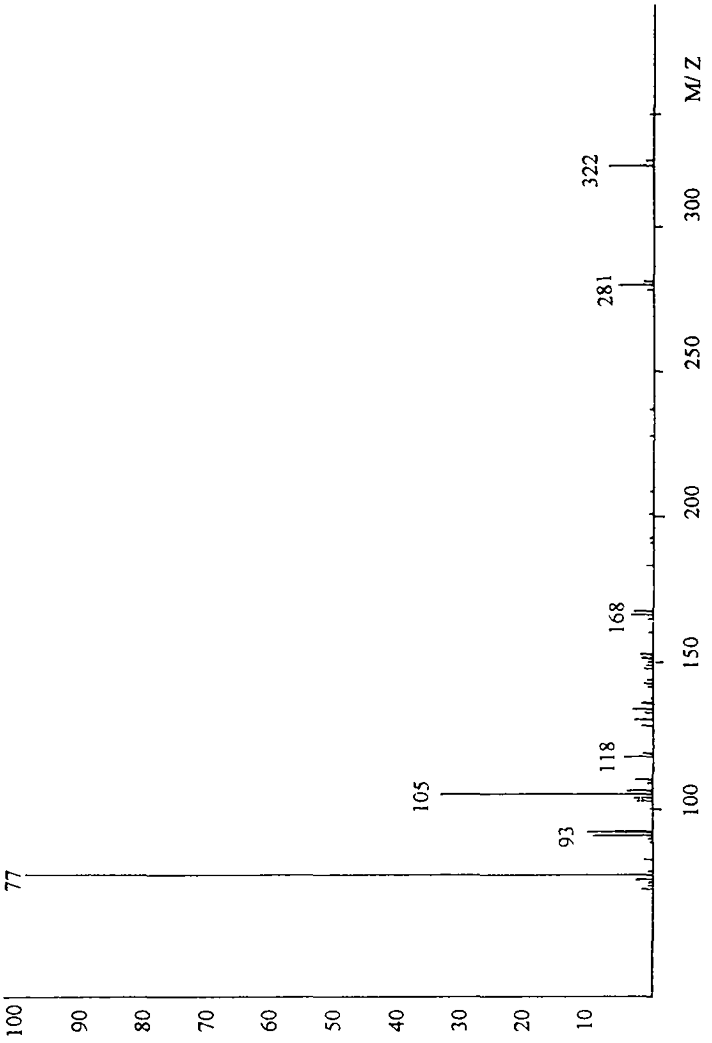


Fig. 2. Mass Spectrum of H_2L {m/z (%): 340.076 (14), 322 (51), 168 (35), 118 (43), 105 (71), 93(59), 77(103)}

The IR spectral data of H_2Dz and the vic-dioxime (H_2L) are summarized in Table II. The disappearance of the N-H and S-H stretching bands, along with the appearance of new absorptions at 3250 cm^{-1} for O-H stretching, 1630 cm^{-1} C=N stretching and 975 cm^{-1} N-O stretching are in agreement[23-27,32-43] with the structure in Fig. 1. The aromatic C-H stretching vibrations were at 3050 cm^{-1}. Furthermore, the C=N stretching vibration frequency of H_2Dz and H_2L was at 1590 cm^{-1}.

IR Spectra and Magnetic Susceptibility of the Complexes

Elemental analyses, IR spectroscopy and magnetic susceptibility were employed to determine the structural characteristics of the complexes (Tables I and II). The reaction of H_2L with Ni(II), Co(II) and Cu(II) salts gives products with the metal-ligand ratio of 1:2, (Fig. 3). For Ni(II), Co(II) and Cu(II), only mononuclear complexes were obtained even when the metal ions were used in excess[24,25] (Table I). Since a distinct lowering in the pH of the solution was observed during the complex formation, deprotonation of the ligand with subsequent N,N'-chelation with the vic-dioxime groups probably occurs. The usual hydrogen bridges (H-O···H) of the square-planar vic-dioxime complexes are characterized by the weak deformation bands[23-27,32-42] around 1750-1720 cm^{-1} in the case of $[Ni(HL)_2]$, and $[Cu(HL)_2]$; but the Co(II) complex had two coordinated water molecules. Consequently, an octahedral structure for the Co(II) and a square-planar structure for the Ni(II) and Cu(II) compounds are proposed (Fig. 3), (Table II). In the IR spectra in Table II of the ligand and complexes, the shifts of the C=N stretching frequency to lower frequency and the vibration of the N-O band to higher frequency indicated the formation of coordination bonds between the metal and nitrogen atoms of the ligands. In the case of the Co(II) complexes, the coordinated H_2O groups are identified by a broad OH absorption at around 3550 cm^{-1} which keeps its intensity even after heating at 110° C for 24 h.

H_2L reacts with Zn(II), Cd(II) and Hg(II) salts to give 1:1 metal-ligand ratio complexes with two of four coordination sites on the metal occupied by the N atom of the oxime groups and the other by an O atom. A chloride ion and a water molecule are also coordinated to the metal ion in $\{[(HL)Cl(H_2O)M]\}$ (Fig. 4). The physical data and IR spectra are consistent with such a structure[23-26,38] (Tables I and II).

Table I. Analytical and Physical Data for H_2L and its Complexes

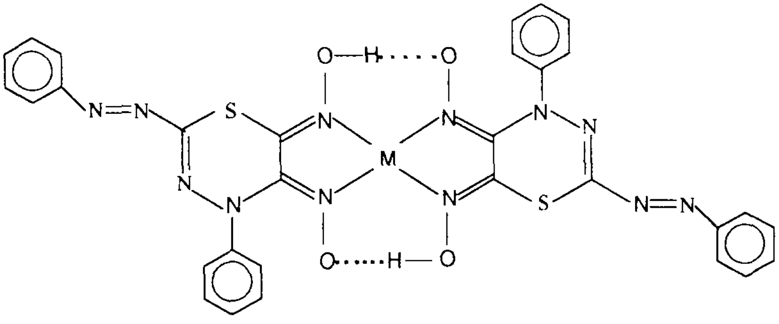
Compound	Formula Weights	Color	M.p.[a] (° C)	Yield (%)	Analysis[b] (%)				
					C	H	N	M	Cl
H_2L	340.0742	orange	128-130	95	52.93	3.56	24.71	-	-
$C_{15}H_{12}N_6O_2S$					(52.99)	(3.52)	(24.72)		
$[(HL)_2Ni]$	736.0681	red	>300	97	48.87	3.01	22.97	7.96	-
$C_{30}H_{22}N_{12}O_4S_2Ni$					(48.96)	(3.05)	(22.91)	(7.93)	
$[(HL)_2(H_2O)_2Co]$	773.0871	Brown	>300	88	46.57	3.39	21.73	7.62	-
$C_{30}H_{26}N_{12}O_6S_2Co$					(46.76)	(3.21)	(21.70)	(7.93)	
$[(HL)_2Cu]$	741.0624	Brown	228-230	79	48.55	2.99	22.64	8.56	-
$C_{30}H_{22}N_{12}O_4S_2Cu$					(48.53)	(3.07)	(22.70)	(8.45)	
$[(HL)Cl(H_2O)Zn]$	455.9749	red	248-250	77	39.32	2.86	18.34	14.27	7.74
$C_{15}H_{13}N_6O_3SClZn$					(39.36)	(2.92)	(18.38)	(14.23)	(7.69)
$[(HL)Cl(H_2O)Cd]$	505.9492	red	242-243	75	35.66	2.59	16.63	22.25	7.02
$C_{15}H_{13}N_6O_3SClCd$					(35.68)	(2.64)	(16.66)	(22.33)	(7.16)
$[(HL)Cl(H_2O)Hg]$	594.0147	red	202-204	74	30.36	2.21	14.16	33.80	5.97
$C_{15}H_{13}N_6O_3SClHg$					(30.21)	(2.25)	(14.23)	-	(5.85)

[a]With decomposition. [b]Calculated values are given in parentheses.

Table II. Magnetic Moments of the Complexes and Characteristic IR Bands (cm^{-1}) of H_2L and the Complexes (KBr pellets)

Compound	Magnetic Moment (B.M.)	υ(N-H)	υ(O-H)	υ (O-H···O)	υ(C=N) *oxime*	υ(C=N)	υ(N=N)	υ(C-N)	υ(N-N)	υ(N-O)	υ(M-L)[a]	υ(H_2O)
H_2Dz	-	3160-3120(b)	-	-	-	1590(s)	1410(m)	1260(m)	1140(m)	-	-	-
H_2L	-	-	3250(b)	-	1630(s)	1590(s)	1410(m)	1250(m)	1150(m)	970(s)	-	-
$[(HL)_2Ni]$	Diamagnetic	-	-	1750-1720(w)	1610(m)	1590(s)	1410(m)	1220(m)	1140(m)	1000(w)	470(w)	-
$[(HL)_2Co]$	1..91	-	-	1720(w)	1610(m)	1580(s)	1390(m)	1205(m)	1125(m)	1000(w)	465(w)	3550(vs)
$[(HL)_2Cu]$	1..52	-	-	1720(w)	1625(m)	1570(s)	1390(m)	1200(m)	1125(m)	1000(w)	450(w)	-
$[(HL)Cl(H_2O)Zn]$	Diamagnetic	-	3240(b)	-	1630(m)	1565(s)	1390(m)	1195(m)	1125(m)	990(w)	520(w)	3430(b)
$[(HL)Cl(H_2O)Cd]$	Diamagnetic	-	3240(b)	-	1625(m)	1565(s)	1380(m)	1200(m)	1125(m)	980(w)	520(w)	3430(b)
$[(HL)Cl(H_2O)Hg]$	Diamagnetic	-	3240(b)	-	1625(m)	1570(s)	1375(m)	1195(m)	1125(m)	985(w)	520(w)	3430(b)

[a] M-L for M = Ni, Co or Cu and L = N; for M = Zn, Cd or Hg and L= O; υ(C-H) = 3050 cm^{-1} for all of the compounds.
b = broad, s = strong, vs = very strong, m = medium, w = weak.



OH_2
Fig. 3. Structure of $[M(HL)_2]$; M = Ni(II), Cu(II) or Co(II)
OH_2

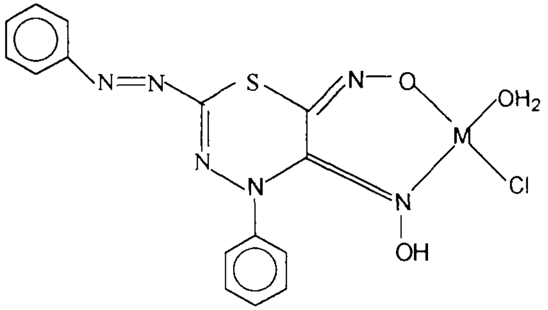


Fig. 4. Structure of $[(HL)Cl(H_2O)M]$ {M = Zn(II), Cd(II) or Hg(II)}

In the region below 700 cm^{-1} several groups of bands appear, all of them are more or less sensitive to the central metal atom. Metal-nitrogen stretching frequencies are reported by a number of workers to occur in the 300-600 cm^{-1} region[44]. The presence of a number of bands or shoulders in a rather narrow range makes difficulty an unambiguous assignment of this vibration to M-N, M-O and M-Cl, in particular for $[(HL)Cl(H_2O)Zn]$, $[(HL)Cl(H_2O)Cd]$ and $[(HL)Cl(H_2O)Hg]$. An empirical assignment for the other metal-nitrogen stretching vibration which is expected to appear in the far-infrared region for these molecules may be proposed: bands at 470, 465, 450 cm^{-1} for $[(HL)_2Ni]$, $[(HL)_2Co]$ and $[(HL)_2Cu]$,respectively, may be assigned to this mode.

The common features of the complexes of H_2L are their insolubility that also hindered spectral investigations of their solutions. Magnetic susceptibility measurements provide sufficient data to characterize the structures (Table II). The mononuclear complex $[Ni(HL)_2]$ is diamagnetic as expected for a d^8 metal ion in a square-planer field[25,26,34,35,40-42]. The magnetic moment of $[Co(HL)_2]$ and $[Cu(HL)_2]$ at 20° C are 2.45 and 1.52 B. M., respectively; the mononuclear complexes $[(HL)Cl(H_2O)Zn]$, $[(HL)Cl(H_2O)Cd]$ and $[(HL)Cl(H_2O)Hg]$ are diamagnetic as expected for d^{10} metal ions in a tetrahedral field[25,26].

EXPERIMENTAL

anti-Dichloroglyoxime[45,46] and cyanogen-di-N-oxide[19] were prepared according to the referenced procedures. The UV-Visible spectra were recorded on a 160 A Shimadzu spectrophotometer. The ^1H NMR spectra were recorded on a Bruker 200 MHz spectrometer. Infrared spectra were obtained on a Unicam Mattson 1000 (FT-IR) spectrometer. Mass spectra were recorded on a Kratos MS 12 Mass Spectrometer, at 70 eV and 220° C ion source temperature (obtained at the University of Glasgow). The magnetic moments of the complexes were measured by the Gouy method with a Newport Instruments type D-104 magnet power supply (293 K). The metal contents of the complexes were determined by a Varian-Faction A-175 type atomic absorption spectrophotometer in solutions prepared by decomposing the compounds in aqua regia and then subsequently digesting in concentrated HCl.

2,3-Hydroxyimino-4-phenyl-6-phenlyazo-1-thia-4,5-diaza-cyclohexa-5-diene (H_2L)

A solution of 2.56 g (10 mmol) of dithizone (3-thioxo-1,5-diphenylformazan, H_2Dz) dissolved in 50 mL of dichloromethane was cooled to -15° C. A solution of cyanogen di-N-oxide in 50 mL dichloromethane, which was prepared from (1.57 g, 10 mmol) anti-dichloroglyoxime and 120 mL N Na_2CO_3 solution, was added to the solution of H_2Dz. After the addition was complete, the solution was stirred at -15° C for 12 hours, the resulting orange compound was separated, filtered and washed with dichloromethane and then dried in vacuo. Yield 3.23 g; UV-Visible (in ethanol) λ_{max} = 436 (ε_1 = 1068), 305 nm (ε_1 =

862.23), 218 nm (ε_1 = 1012); ^{1}H NMR (in DMSO-d_6) δ = 12.53 (s, 1 H, disappears upon deuterium exchange), 12.04 (s, 1 H, disappears upon deuterium exchange), 7.91-714 (m, 10H); ms: m/z 340.076 (14) ($C_{15}H_{12}N_6O_2S$), 322 (51) ($C_{15}H_{10}N_6OS$), 281 (51) ($C_{14}H_{11}N_5S$), 168 (35) ($C_7H_{11}N_3S$), 118 (43) (C_7H_6-N_2), 105 (71) (C_6H_5-N_2)$^+$, 93 (59) (C_6H_5-NH_2), 77 (103) (C_6H_5-) (Fig. 1).

[Ni(HL)$_2$], [Co(HL)$_2$] and [Cu(HL)$_2$] Complexes

A solution of 0.5 mmol of metal salt [$NiCl_2 \cdot 6H_2O$ (119 mg), $CoCl_2 \cdot 6H_2O$ (119 mg) or $CuCl_2 \cdot 2H_2O$ (85 mg)] in 30 mL hot water was added to the suspension of 340 mg (1.0 mmol) H_2L in 50 mL hot ethanol. The color after dissolution changed immediately and a sharp decrease in the pH of the solution to 3.5-4.0 was observed. When the pH was increased to 5.0-5.5 with 0.5% NaOH solution in ethanol, precipitation started. The mixture was further stirred on a water bath at 60° C for 1 h in order to complete precipitation. The precipitates were filtered, washed with hot ethanol and hot water and then dried in vacuo.

[(HL)ZnCl(H_2O)], [(HL)CdCl(H_2O)] and [(HL)HgCl(H_2O)] Complexes

A solution of 1.0 mmol of metal salt [$ZnCl_2 \cdot 2H_2O$ (170 mg), $CdCl_2 \cdot 2H_2O$ (201 mg) or $HgCl_2 \cdot 2H_2O$ (308 mg)] in 30 mL water was added to the suspension of 340 mg (1.0 mmol) H_2L in 50 mL ethanol. The color of the mixture changed immediately and a sharp decrease in the pH of the solution to 1.0-2.0 was observed. When the pH was increased to 5.0-5.5 with 0.5% NaOH solution in ethanol, precipitation started. The mixture was further stirred on a water bath at 60° C for 2 h in order to complete precipitation. The precipitate was filtered, washed with hot ethanol and hot water and then dried in vacuo.

The colors, melting points, yields, elemental analyses, characteristics FT-IR absorptions and magnetic moments of the complexes are give in Tables I and II.

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