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Synthesis And Characterization of Novel Functionalized Tetradentate Ligand Type H_3NS_3 And Its Metal Complexes ith Re(V), Ni(II), Cu(II), Cd(II) & Hg(II)

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Abstract

This work represents the preparation of the tetradentate ligand H_3NS_3 (H_3L) and its metal complexes with rhenium(V), nickle(II), copper(II), cadmium(II) and mercurry(II) metal ions. The ligand and its complexes were characterized when needed by Infrared, Ultraviolet–visible, HPLC, Mass, ^1H nuclear magnetic resonance, and atomic absorption spectroscopic techniques, elemental analysis, and electrical conductivity. The proposed structure for (H_3NS_3) with Re(V) is square pyramidal, with Ni(II) is distorted square planar, and with the rest of metal ions is distorted tetrahedral.

Keywords: Tetradentate ligand (H_3NS_3), Re(V), Ni(II), Cu(II), Cd(II) & Hg(II).

تحضير وتشخيص ليكاند رباعي السن نوع H_3NS_3 ومعقداته مع ايونات Re(V)، Ni(II)، Cu(II)، Cd(II)، و Hg(II)

الخلاصة

تضمن البحث تحضير ليكاند رباعي السن (H_3L) نوع (H_3NS_3) مع أيونات Re(V)، Ni(II)، Cu(II)، Cd(II) و Hg(II). شخصت المركبات والمعقدات حسب الحاجة بواسطة طيف الأشعة تحت الحمراء، طيف الأشعة فوق البنفسجية والمرئية، تقنية (HPLC)، طيف الكتلة، طيف الرنين النووي المغناطيسي، طيف الامتصاص الذري، التحليل الكمي الدقيق للعناصر وكذلك قياس التوصيلية الكهربائية. بينت الدراسات ان الشكل الفراغي المتوقع لمعقد الرينيوم الخماسي مع H_3L هو هرم مربع القاعدة، مع Ni(II) هو مربع مستو مشوه ومع الأيونات الأخرى هرم رباعي مشوه.

Introduction

New tetradentate ligands having three negative charges of the type (H_3NS_3) containing amide and amine groups have been prepared in basic medium by loosing three protons [1]. These ligands were used to prepare new complexes of Tc(IV) and Re(V) with the general formula: $[TcO(NS_3)]^-$, $[ReO(NS_3)]$ using $[MOCl_4]^-$ and $[ReOCl_3(PPh_3)_2]$ or $[ReO_2(Py)_4]Cl$ as starting materials in the reaction, where [M= Tc, Re]. Some complexes of the oxo-Re(V) with new tetradentate ligands of the type (H_3NS_3); N(phenylthiocarbamido)-N'-(1-

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mercapto-2- thiapentanoyl) hydrazine & N(phenylthiocarbamido)-N'-(1-mercapto-3-methyl-2-thiapentanoyl) hydrazine were reported [2]. These ligands were reacted with the complex $[ReO_2 (Py)_4]Cl$ using THF as a medium for the reaction in the presence of triethylamine as a base. The IR spectrum shows a strong absorption band at 965 cm^{-1} due to the stretching of υ(R=O) group. The proposed structure for the complex is square pyramidal.

Some complexes of Ni(II) were prepared using tetradentate ligands with the general formula $K[Ni(NS_3]$ [3]. Comba and coworkers [4] prepared the square planar complex [(6-methyl-6- nitro-1, 11-dithia-4, 8-diazacyclotetradacane) Copper(II)] [perchlorate]. Other complexes with the general formula $[MLX_2]$, M = Zn(II), Cd(II), and Hg(II) were prepared by reaction of metal ions with the ligands tetramethyl dithiooxamide and tetraethyl dithiooxamide, where X= Cl, Br, I [5].

Experimental: All the chemicals were of high purity and used without further purifications.

Instruments: Stuart Melting Point Apparatus; Pye-Unicam SP3-300; Shimadzu UV-160A Ultraviolet Visible Spectrophotometer; HPLC Shimadzu LC-6A (koyota-Tapan), Shimadzu GC-Mass 1000 P; Hitachi Perkin Elmer R-24B 60 MHZ NMR Spectrometer; Perkin Elmer 240B Elemental Analyzer; Shimadzu AA 680G; Titroprocessor–665 Dosimat-Metrohm Swiss; Phillips PW9 526 Conductivity Meter; density function theory was used for calculating bond lengths and bond angles.

Preparation of Compounds:

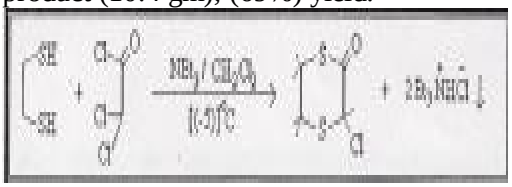
1. Preparation of $[ReOCl_3(PPh_3)_2]$: Trichloro oxobis-(triphenylphosphine) rhenium(V):

To a round bottom flask containing (0.5 gm, 2.7 mmol) of rhenium metal which was immersed in an ice bath, 9 ml of 30% H_2O_2 was added gradually with stirring. When the addition was complete, the solution in the flask was evaporated nearly to dryness (1 – 2) ml. The flask returned to the ice bath where a mixture of (5 ml 37% HCl and 5 gm, 1.9 mmol PPh_3 dissolved in 25 ml acetone) was added gradually with continuous stirring where a green to yellow precipitate was formed. The flask removed from the ice bath and the contents in the flask were refluxed for 90 minutes. The mixture was allowed to cool for an hour, filtered and the precipitate washed with 10 ml ethanol and left to dry. Yield 2.2 gm (2.64 mol), 98%; m. p. = 213^oC.

2. Preparation of compound (A): 3-Chloro-2-oxo-1, 4-dithiacyclohexane:

In a three neck round bottom flask (88 mmol) 1, 2-ethanedithiol and (176 mmol) triethylamine were mixed under an inert atmosphere (N_2). The mixture

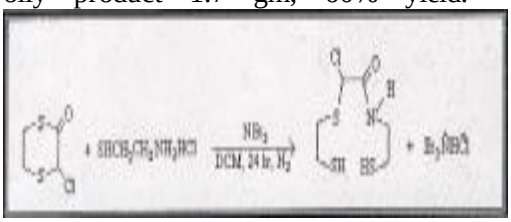
was cooled to (-10°C), then a solution of 88 mmol dichloroacetyl chloride in 100 ml dichloromethane was added drop wise from a pressure equalized funnel with stirring and the temperature was maintained at -5 °C for 90 min., a white precipitate of triethylammonium chloride was formed . The solution was filtered, the filtrate washed with distilled water and the organic layer was separated and dried with anhydrous $MgSO_4$, then the solvent was evaporated under reduced pressure leaving a yellowish-white oily product (10.4 gm); (69%) yield.



3. Preparation of the Ligand H_3NS_3 (H_3L):

N-(β-mercaptoehyl)-2-(β-mercaptoehylthio)-2-chloroacetamide.

11.4 mmol of 2-mercaptoethylammonium chloride in 35 ml dichloromethane (DCM) and (1.6 ml) triethylamine were mixed in a round bottom flask, to this mixture (11.4 mmol) of 3-Chloro-2-oxo-1, 4-dithiacyclohexane (A) in (35 ml) DCM was added dropwise with continuous stirring under nitrogen atmosphere for 24 hrs after which a white precipitate of triethylammonium chloride was formed. The solution was filtered, the organic layer washed two times with distilled water. The organic layer was separated and dried over anhydrous $MgSO_4$, filtered, the solvent was evaporated leaving a yellowish-white oily product 1.7 gm; 60% yield.



4. Preparation of the complex [ReO(L)]:

In a round bottom flask under inert atmosphere; (4 mmol) of H_3NS_3 in 15 ml DCM, 25 ml (1 M) sodium acetate and 20 ml methanol were mixed. To this mixture (4 mmol) of solid $[ReOCl_3(PPh_3)_2]$ was added with stirring. The solution was refluxed for (2 hrs), cooled, filtered and the solvent was evaporated under reduced pressure to dryness. Fifty milliliters of DCM was added and the solution filtered, washed two times with distilled water. The organic layer was separated, dried with anhydrous $MgSO_4$ and the volume was reduced to 5ml. After that 15 ml of n-hexane was added where a red-brown precipitate formed (0.11 gm); (61%) yield, m. p. = 110°C.

5. General procedure for the preparation of [M(HL)] complexes:

(6 mmol) of H_3NS_3 in 20 ml (1:1) dichloromethane and methanol was put in a 100 ml round bottom flask; potassium hydroxide solution was added to raise the pH to (8-9). To this

mixture (6 mmol) of metal salt in 20 ml methanol was added dropwise under nitrogen atmosphere with stirring. The solution was refluxed for 90 minutes where a precipitate was formed. The mixture was cooled, filtered, and the precipitate washed with 5 ml methanol then with 10 ml ether and vacuum dried.

Results and Discussion:

Characterization of compound A (3-Chloro-2-oxo-1,4-ithiacyclohexane):

This compound was prepared in 1993 by Larsen and co-workers by two steps [7]. In this work it was prepared by a new method in one step through the direct reaction between 1,2-ethanedithiol and dichloroacetyl chloride using dichloromethane and triethylamine as a reaction medium. The new method took less time giving the same yield and less expensive. It was characterized by HPLC, mass spectrometry (table 1), UV-Vis. (table 3), IR (table 4), (C.H.N.S) (table 5) and ^{1}HNMR.

The HPLC chromatogram shows one absorption band at 254 nm with retention time (R_t=4.8 min.) indicating that this compound is pure and occurred as one isomer in solution. The electron impact mass gave the fragments as shown in (table 1) which are compatible with the mentioned compound. The ultra violet-visible spectrum (table 3) shows one absorption band at (279.5 nm) which is due to and (π - π^*) transition. Table (4) shows the IR bands and their characterization. The ^{1}HNMR spectrum of this compound shows two chemical shifts, the first triplet at (δ = 2.4 – 2.7 p.p.m.) due to the protons of the CH_2 group, while the second singlet at (δ = 3.28 – 3.1 p.p.m.) which is due to the proton of (Cl-CH) group.

Characterization of the ligand H_3NS_3:

This tetradentate ligand of the type (H_3NS_3) was prepared as mentioned in the experimental section. Different spectral techniques were used to characterize this ligand and some of the data are reported in tables (2), (3), (4) and (5). The UV-visible spectrum for the ligand (H_3NS_3) shows one absorption band at (270 nm) which is due to (π - π^*) transition.

The ultra violet visible spectra:

The absorption bands for the complexes will help to give an idea of their structure [8]. Table (3) shows the (UV–Vis) bands for the ligand (H_3NS_3) and its metal complexes. **[H_3NS_3]** gave a band at 270 nm due to (π-π^*) transitions. **[ReO(L)]** spectrum shows three absorption bands, the first at 280 nm which is longer in wavelength than that for the ligand by 10 nm due to (M–L) coordination. The second band at 396 nm may be due to (d–d) electronic transition and this peak withdrawn to shorter wavelength due to (intensity stealing) and its origin is due to ($^1E \rightarrow {}^1B_2$) transition. The third absorption band appeared at 558.5 nm is due to d

– d transition and its origin ($^1E \rightarrow {}^1A_1$) transition [9].

[Ni(HL)] shows three absorption bands, the first at 301 nm which is longer in wavelength than that of the ligand by 31 nm due to (M–L) coordination. The second band at 347 nm is due to d–d transition assigned ($^1A_{1g} \rightarrow {}^1B_{1g}$). The third band at 558.5 nm is due to ($^1B_{2g} \rightarrow {}^1B_{1g}$) transition [10,11]. **[Cu(HL)]** shows two bands, the first at 291 nm due to (M–L) coordination and the second band at 681 nm is due to ($^2B_2 \rightarrow {}^2E$) which is broad due to Jan-Teller distortion [12-14]. **[Cd(HL)]** and **Hg(HL)] complexes** show two bands (table 3), the first at 260 nm due to (M–L) coordination and the second bands at (277 & 278.5) nm which are due to charge transfer.

The IR spectra for the ligand H_3NS_3 (H_3L) and its complexes

Tables (4) list the IR bands for the H_3NS_3 ligand and its complexes. The IR spectrum of the ligand shows two bands at (3280 cm^{-1} & 2540) cm^{-1} which are due to the stretching vibration frequencies of υ(N-H) and υ(S-H) bonds respectively. On the formation of the complex [ReO(L)], these bands were disappeared. In this complex, the band appeared at 1660 cm^{-1} which is due to υ(C=O) is shifted from that of the ligand (1630 cm^{-1}) by 30 cm^{-1} an indication of coordination of the ligand to rhenium metal. The second band which appeared at 960 cm^{-1} is due to υ(Re=O), while the third band appeared at 580 cm^{-1} is due to υ(Re-N) bond [15]. The fourth band appeared at 330 cm^{-1} is due to υ(Re-S) bond [16].

For the rest of complexes, the absorption bands are listed in the above table.

Tables (5) show the (C.H.N.S) analysis data and some physical properties for the prepared complexes.

Molar Conductivity

The molar conductivity for the complexes is used to observe the behavior of these compounds in solution (molecules or ions) [17,18]. Dimethyl formamide and dimethyl sulfoxide were used as solvents in which the concentration of the solution (10^{-3} M) at room temperature. These studies show that all the complexes in solution are non conducting (table 6).

The molecular structure of Rhenium(V) complexe with H_3NS_3 ligand

According to the results found from the characterization of [ReO(L)], the proposed molecular structure for the complex is square pyramidal where rhenium has (+5) oxidation state. Figure (1) show the expected molecular structure for [ReO(L)] complex where rhenium metal coordinate to the H_3NS_3 ligand (after loosing three protons) through three negatively charged atoms (two sulfur and one nitrogen) and one lone pair belong to another sulfur atom (thio-

ether) where the oxo-group on the top of the pyramid. Table (7) shows the bond lengths and bond angles for the complexes which were calculated using the density function theory.

The proposed molecular structure for [Ni(HL)] complex

According to the data collected on this complex, the proposed molecular structure is distorted square planar depending on the bond lengths and bond angles for comparable systems as shown in table (8). The proposed structure for the complex is shown in figure (2) where nickel is coordinated to H_3NS_3 ligand (after loosing two protons) through (two negatively charged sulfur atoms) and two lone pairs; one from nitrogen and the other from the third sulfur atom (thio-ether).

The proposed molecular structure for [Cu(HL)], [Cd(HL)] & [Hg(HL)] complexes

From the measured data, the proposed molecular structure for the mentioned complexes is distorted tetrahedral depending on bond lengths for comparable systems as shown in table (9) [19-20]. Figure (3) show the coordination of copper cadmium and mercury to H_3NS_3 ligand where the coordination mode is similar to that of nickel complex.

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Table (1) The Fragments Of Compound (A)

Fragments	Mass/ charge	Relative abundant
M^+	169	3.77
$[M-(OC-Cl)]^+$	105	100
$[M-(C-OC-Cl)]^+$	93	4.24
$[M-(S-CH_2CH_2-S-H)]^+$	76	5.66
$[M-(CH_2CH_2-S-CHCl)]^+$ or $[M-(CH_2CH_2SCH-Cl)]$	60	35.8
$[M-(CH_2-CH_2-S-OC-Cl)]^+$	45	33.9
$[M-(CH_2-CH_2-S-OC-CH-Cl)]^+$	32	34.9

Table (2) The Fragments of The Ligand (H_3NS_3)

Fragments	Mass/ charge	Relative abundant
M+	246	1.96
[M-(Cl)]+	211	3.92
[M-(HC-Cl)]+	198	42.15
[M-(CO-NH-CH2 CH2-SH)]+	142	18.62
[M-(S-CH2CH2-S-CH-Cl)]+	105	100
[M-(H-SCH2-CH2-S-CH-Cl-C)]+	92	68.62
[M-(SH-CH2CH2-S-NH-CH2CH2SH)]+	77	6.86
[M-(SH-CH2CH2-S-CO-NH-CH2CH2SH)]+	49	50.98

Table (3) The (UV-Vis) Absorption Bands And The Molar Absorptivity For The Ligand (H_3NS_3) And Its Complexes

Compound	λ (nm)	ν (cm^{-1})	ε ($l.\ mol^{-1}.\ cm^{-1}$)
A	279.5	35778	1234
H_3NS_3 (H_3L)	270	37037	1490
[ReO(L)]	280	35714	1949
	396	25252	733
	558.5	17905	109
[Ni(HL)]	301	33222	1667
	347	28818	900
	558	17921	430
[Cu(HL)]	291	34364	2491
	681	14684	238
[Cd(HL)]	260	38461	464
	277	36101	803
[Hg(HL)]	260	38461	540
	278.5	35906	1131

Table (4) The IR Absorption Bands For Comp. (A) & (H_3NS_3) And Its Complexes In Cm^{-1}.

N(Re=O) = 960 (S), **N(S-H)** = 2540 (M-W)

Formula	ν(C-H)	ν(C=O)	δ(N-H)	δ(C-H)	Additional peaks
A	2920 (m)	1660 (vs)	-	1440 (s)	1260 δ(C-H) (w), 1060 (s) ν(C-S), 660 ν(C-Cl) (w)
H_3NS_3	2900 (m)	1630 (s)	1520 (s)	1460 (m)	3280(s) (br.) ν(N-H), 3060 (overtone amide(II) band, 650 ν(C-Cl) (br.), 480 δ(N-C=O) (w)
[ReO(L)]	2940 (w)	1660 (s)	-	1460 (m)	1270 ν(C-N), 670 ν(C-Cl) (s), 580 ν(Re-N) (m), 330 ν(Re-S) (s)
[Ni(HL)]	2923 (w)	1658 (s)	1522 (m)	1404 (m)	3313 ν(N-H) (w), 827 δ(N-H) (w), 430 ν(Ni-S) (w)
[Cu(HL)]	2920 (w)	1660 (s)	1520 (m)	1390 (m-w)	830 δ(N-H) (w), 480 δ(N-C=O) (w)
[Cd(HL)]	2940 (w)	1660 (m)	1520 (w)	1410 (w)	680 ν(C-Cl) (w)
[Hg(HL)]	2910 (w)	1660 (w)	1500 (m)	1410 (w)	1260 ν(C-N) (w), 660 ν(C-Cl) (br), 500 ν(Hg-N) (w)

Table (5) The Elemental Analysis Data & Some Physical Properties For The Ligands & Complexes: ( ) Calculated

Formula	Solubility	M. P. (^oC)	M. Wt.	Micro Analysis				
				% Metal	% C	% H	% N	% S
A	DCM	oily	168.48		(28.48) 27.7	(2.98) 2.8		(38.02) 37.6
H_3NS_3	DCM	oily	245.82		(29.31) 28.4	(4.92) 5.3	(5.69) 4.7	(39.13) 38.3
[ReO(L)]	DMF, DMSO, CH_2Cl_2, $C_2H_4Cl_2$	110	445	(41.84) -	(16.19) 16.05	(2.03) 2.01	(3.14) 3.12	
[Ni(HL)]	DMF, DMSO	> 300	302.50	(19.40) 18.90	(23.82) 23.94	(3.33) 3.28	(4.63) 4.70	
[Cu(HL)]	DMF, DMSO	170 (dec.)	307.33	(20.67) 21.32	(23.44) 23.21	(3.27) 3.31	(4.55) 4.60	
[Cd(HL)]	DMF, DMSO	215 (dec.)	356.21	(31.55) 32.10	(20.23) 19.95	(2.82) 2.95	(3.93) 3.77	
[Hg(HL)]	DMF, DMSO	160 (dec.)	444.39	(45.13) -	(16.21) 16.31	(2.26) 2.19	(3.15) 3.2	

Table (6) The Molar Conductivity Data For The Complexes (Concentration = 10^{-3} M At 25°c), Molar Conductivity In ($S.Cm^2.Mol^{-1}$)

Complex	Solvent	Molar Conductivity
[ReO(L)]	DMF	9.2
[Ni(HL)]	DMF	33.9
[Cu(HL)]	DMSO	13.7
[Cd(HL)]	DMSO	21.9
[Hg(HL)]	DMSO	6.4

Table (7) Bond Lengths and Bond Angles For [ReO(L)] Complex

Type of Bond	Length in Angstrom	Type of Angle	Angle in Degree
Re – S1	2.19	**S2 – Re – S3**	164.45
Re – S2	2.11	**O – Re – S1**	102.14
Re – S3	2.12	**O – Re – S2**	100.71
Re – O	1.59	**O – Re – S3**	94.73
Re – N	2.00	**O – Re – N**	108.61
C – Cl	1.90		

Table (8) Bond Lengths and Bond Angles For [Ni(HL)] Complex

Type of Bond	Length in Angstrom	Type of Angle	Angle in Degree
Ni – S1	2.18	**N1 – Ni – S2**	93.19
Ni – S2	2.06	**N1 – Ni – S3**	86.81
Ni – S3	2.11	**S1 – Ni – S2**	82.21
Ni – N	1.88	**S1 – Ni – S3**	97.79

Table (9) Bond Lengths and Bond Angles For [Cu(HL)] Complex

Type of Bond	Length in Angstrom	Type of Angle	Angle in Degree
Cu – S1	2.17	**N1 – Cu – S2**	98.89
Cu – S2	2.10	**N1 – Cu – S3**	88.19
Cu – S3	2.13	**S1 – Cu – S2**	92.56
Cu - N	1.78	**S1 – Cu – S3**	114.39

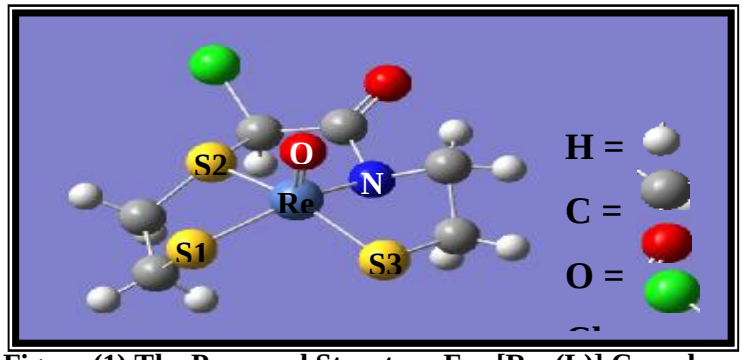

Figure (1) The Proposed Structure For [Reo(L)] Complex

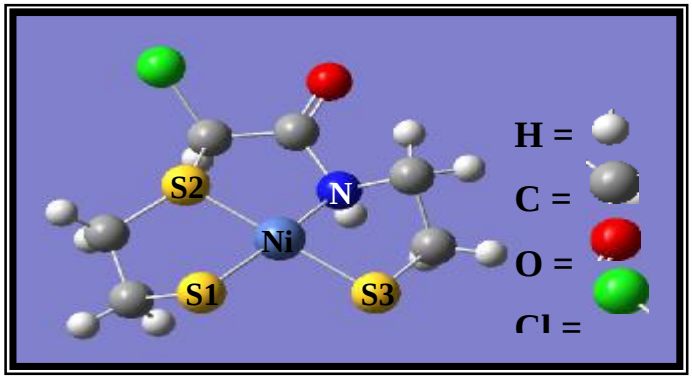

Figure (2) The Proposed Structure For [Ni(HL)] Complex

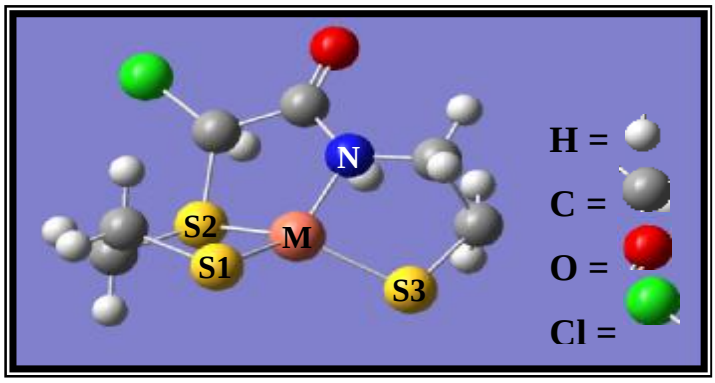

Figure (3) The proposed structure for [Cu(HL)], [Cd(HL)] & [Hg(HL)] complexes