

New rhenium and zinc complexes of 2-formylpyridine *N*(4)-phenylthiosemicarbazone

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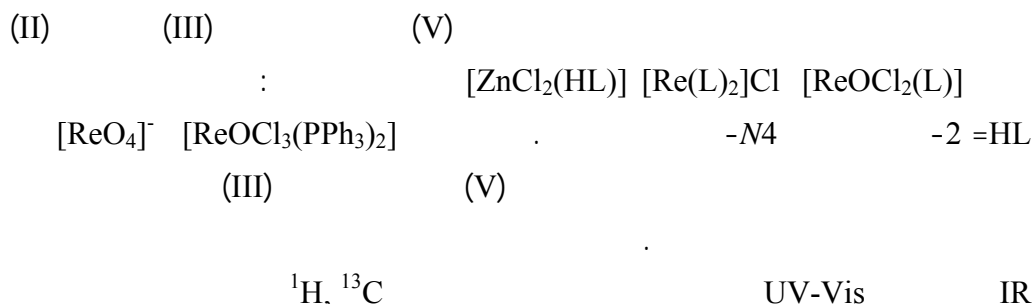
(NJC)

(Received on 11 / 4 / 2006)

(Accepted for publication on 19/8 / 2006)

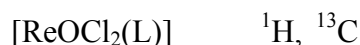
Abstract

A New rhenium(V)-oxo, rhenium(III) and Zn(II) complexes $[\text{ReOCl}_2(\text{L})]$, $[\text{Re}(\text{L})_2]\text{Cl}$ and $[\text{ZnCl}_2(\text{HL})]$ (where; HL = 2-formylpyridine-*N*(4)-phenylthiosemicarbazone) have been synthesised and characterised. $[\text{ReOCl}_3(\text{PPh}_3)_2]$ and $[\text{ReO}_4]^-$ in presence of PPh_3 have been used as a starting material to prepare rhenium(V)-oxo and rhenium(III) complexes, while ZnCl_2 is used to prepare the zinc complex. The new complexes have been characterised by microanalyses, IR, (UV-Vis.), ^1H , ^{13}C NMR, mass spectroscopy and molar conductance. These studies show the Re(III) ion is in a distorted octahedral environment with two tridentate deprotonated thiosemicarbazone binding as monoanionic ligands through the sulfur, pyridyl nitrogen and azamethinic nitrogen in which the complex does not result in isomeric mixtures. The geometry about Re(V) ion is a distorted octahedral environment with one tridentate deprotonated monoanionic ligand, two chloro ligands and oxo moiety. The NMR studies (^1H , ^{13}C) of $[\text{ReOCl}_2(\text{L})]$ show the existence of the complex in two isomers in solution. On the other hand the geometry about Zn is a trigonal bipyramidal with one tridentate ligand in thion form, and two chloro ligands.



(III)

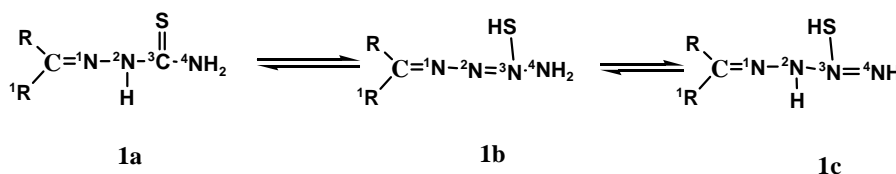
(V)



Introduction

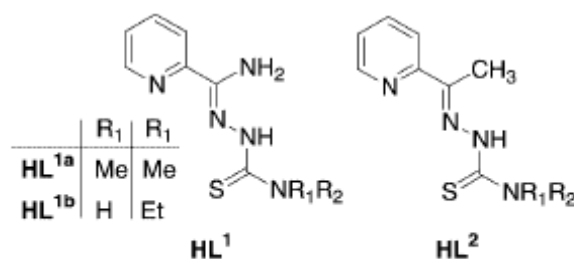
Thiosemicarbazones compounds exhibit a wide range of biological activity, which is dependent upon the chemical nature of the moiety attached to the C-S carbon atom.^[1] In particular heterocyclic thiosemicarbazones display very interesting biological properties, such as antitumour, antibacterial and antifungal activity.^[2] The activity of the uncomplexed thiosemicarbazone can be increased significantly by the formation of metal complexes, as has been demonstrated previously in literatures.^[3-5]

Thiosemicarbazones (tautomeric forms **Ia**, **Ib** and **Ic**) are versatile ligands which can coordinate as neutral ligands or in their deprotonated form. Numerous metal complexes have been studied chemically and by X-ray crystallography.^[6] Ligands with additional donor groups such as phosphines, amines, hydroxyl or thiol group at the residue R¹ are of special interest since they can coordinate in a tridentate manner which results in a significant increase of the stability of the complexes.^[7]



Rhenium complexes with thiosemicarbazones are rare due to their stability. The first structural report on such compounds was published dealing with cationic ReIII compounds of the general composition $[\text{Re}(\text{L})_2]^+$, where: L represents a tridentate 2-acetylpyridine which the two nitrogen atoms of the hydrazones unit bind to each one of the rhenium atoms. They have been

prepared by a reductive ligand exchange starting from $[\text{ReOCl}_3(\text{PPh}_3)_2]$ or $[\text{ReO}_4]^-$.^[8] A recent publication reported that, reduction of the metal ion can be avoided and stable rhenium(V) oxo complexes are formed when 2-pyridineformamidethiosemicarbazones (HL^2) are used instead of HL^1 . X-ray crystallography showed the geometry about Re(V) is a distorted octahedral.^[9]



Experimental

Reagents were purchased from Fluka and Redial – Dehenge Chemical Co. I.R spectra were recorded as (KBr) discs using a Shimadzu 8300 FTIR spectrophotometer in the range (4000-400) cm^{-1} . Electronic spectra of the prepared compounds were measured in the region (200-900) nm for 10^{-3} M solutions in (DMSO) at 25°C using a Shimadzu 160 spectrophotometer, with $1.000 \pm 0.001 \text{ cm}^2$ matched quartz cell. Mass spectrum for the ligand was

obtained by Electron-Impact (EI), while rhenium complexes were recorded on a VG autospec micromass spectrometer operating under fast atom bombardment conditions (nitrobenzyl alcohol matrix). The spectra were recorded at University of Free Berlin/Germany, and Queen Mary, University of London/UK. Nuclear magnetic resonance spectra (^1H , ^{13}C -NMR) were acquired with Bruker 400, and Jeol EX400, EX270 Hz spectrometers in DMSO-d_6 . The spectra were recorded at University of Free

Berlin/Germany, and Queen Mary, University of London/UK. Elemental microanalyses were performed on a (C.H.N.) analyser from Heraeus (Vario EL), at the University of Free Berlin/Germany. The chloride contents for complexes were determined by using potentiometer titration method on (686–Titro processor– 665Dosimat–Metrohm Swiss).Electrical conductivity measurements of the complexes were recorded at 25°C for 10⁻³ M solutions of the samples in (DMSO) using a PW 9526 digital conductivity meter.

Synthesis

[ReOCl₃(PPh₃)₂] was prepared by a literature procedure.^[10] The ligand [HL] was synthesised by conventional procedure^[11]: 2-formylpyridine (3.0g, 28mmol) and 4-phenylthiosemicarbazide (4.65g, 28mmol) were added to methanol (20mL). The mixture was heated at reflux under an atmosphere of nitrogen for 4 hrs. The reaction mixture was allowed to cool to room temperature. A crystalline precipitate formed which was collected by filtration and washed with a small amount of cold methanol and copious quantities of diethyl ether to give the ligand as large beige crystals, 5.4g (75%).

[ReOCl₂(L)] complex.

[ReOCl₃(PPh₃)₂] (0.162g, 0.194mmol) was added to a mixture of [HL] (0.05g, 0.195mmol) in (20mL) MeOH. The mixture was heated at reflux under an atmosphere of nitrogen for (2-3) hours, during which time the colour of the reaction mixture became brown in colour. The mixture was allowed to cool to room temperature, and filtered off. A red-brick solid was collected, washed with (5mL) cold MeOH and (5mL) Et₂O. Yield (0.06g, 58%) of [ReOCl₂(L)] .

[Re(L)₂]Cl complex. [ReOCl₃(PPh₃)₂] (0.162g, 0.194mmol) was added to a mixture of HL (0.1g, 0.39mmol) in (35mL) MeOH. The mixture was heated at reflux under an atmosphere of nitrogen for 4 hours, during which time the colour of the reaction mixture became brown in colour. The mixture was allowed to cool to room temperature, and filtered off. The solvent of the filtrate was reduced under vacuum to *ca.* (6mL), and a black-brown solid was formed upon addition of (20mL) Et₂O. The precipitate was recrystallised from CH₂Cl₂/n-hexen, to give (0.091g, 63%) of the title compound.

Synthesis of $[\text{Re}(\text{L})_2]\text{Cl}$ from $[\text{NH}_4][\text{ReO}_4]$. $[\text{NH}_4][\text{ReO}_4]$ (0.1 g, 0.373 mmol) was added to a mixture of methanol (20mL), triphenylphosphine (0.4g, 1.52 mmol) and HCl (37 %) (1mL). The mixture was heated at reflux under an atmosphere of argon for 1 hour. The mixture was allowed to cool to room temperature, and triethylamine (1.5mL), (HL) (0.19g, 0.74mmol) in (12 mL) methanol was added. The mixture was heated at reflux under an atmosphere of nitrogen. The mixture was filtered hot and the solvent was reduced to about (8 mL) by evaporation under reduced pressure. The mixture was left to stand at 4 °C overnight. The black-brown crystals were collected by filtration, and washed with cold methanol (1mL) and Et₂O (5 mL) to give $[\text{Re}(\text{L})_2]\text{Cl}$ (0.1g, 37%). Analytical data was consistent with the compound synthesised from $[\text{ReOCl}_3(\text{PPh}_3)_2]$.

$[\text{ZnCl}_2(\text{HL})]$ complex. To a stirred solution of [HL] (0.05g, 0.195 mmole), in methanol (20 ml) was added slowly a solution of ZnCl₂ (0.026g, 0.195mmole) in methanol (10ml). The resulting mixture was heated under reflux for 3 hours under nitrogen atmosphere, during which time the solution became a yellow

in colour, and a precipitate was formed. The solid was collected by filtration, washed with methanol (5mL) and dry ethyl ether (10mL), and dried under vacuum to give 0.063g, (82%) yield of the title compound.

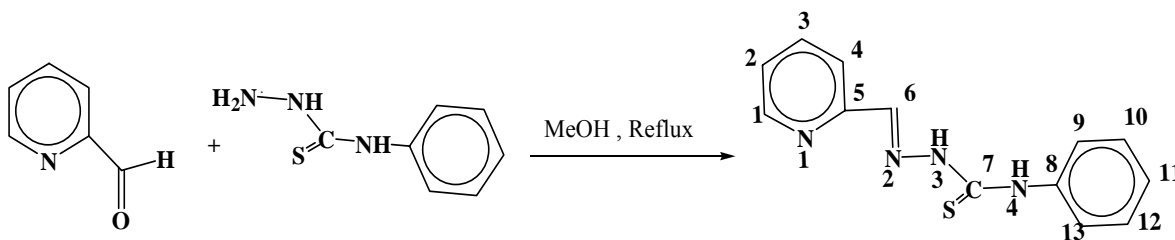
Results and Discussion

Synthesis of the ligand

The Schiff base ligand was prepared by the condensation of pyridine-2-carboxaldehyde with the 4-phenylthiosemicarbazide (**Scheme1**). The ligand was characterised by elemental analysis (**Table1**), IR (**Table2**), (U.V-Vis) (**Table3**), mass spectroscopy, ¹H and ¹³C NMR spectra (**Table4**). The IR spectrum (**Figure1-1**) showed several strong bands at (1596) and (1550, 1496, 1465)cm⁻¹ assigned for $\nu(\text{C}=\text{N})$ imine and $[\nu(\text{C}=\text{N}) \text{ pyr diyl} + \nu(\text{C}=\text{C})]$ stretches respectively. The bands at (3305) and (3120) cm⁻¹ were assigned to $\nu(\text{N}_{(4)}\text{-H})$ and $\nu(\text{N}_{(3)}\text{-H})$ respectively. The latter band indicated the presence of the ligand in the thion form.^[12] The spectrum showed no band around *ca.* (2550)cm⁻¹ that could be related to $\nu(\text{S-H})$. The (U.V.-Vis) spectrum exhibits a highly intense absorption peak at (211 nm) (47393cm⁻¹) ($\epsilon_{\text{max}} = 4410 \text{ molar}^{-1}\text{cm}^{-1}$) and (328nm)

(30407cm⁻¹) (ϵ_{\max} =1720 molar⁻¹cm⁻¹) which were assigned to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions respectively.^[13] Whilst the peak at (391nm) (25575cm⁻¹) (ϵ_{\max} =334 molar⁻¹cm⁻¹) was assigned to charge transfer. ¹H NMR spectrum in (DMSO-d⁶) (**Figure2**) displayed signals at chemical shifts (12.11) and (10.33)ppm attributed to $\delta(N_{(3)}-H)$ and $\delta(N_{(4)}-H)$ respectively. The chemical shift at (8.12)ppm assigned for $\delta(H-$

C=N₍₂₎) imine. ¹³C NMR spectrum showed a signal at chemical shift (176.34)ppm was attributed to (C=S). The EI(+) mass spectrum of the ligand showed the parent ion peak at $m/z= 256$ (M)⁺, and the following fragments; 178= ($M-py$)⁺, 150= [$M-\{py+HC=NH\}$]⁺, 136= [$M-\{py+HC=N-NH\}$]⁺, 92= [$M-\{py+HC=N-NH-C=S\}$]⁺, 77= [$M-\{py+HC=N-NH-C=S-NH\}$]⁺.^[14]



Scheme (1) The synthesis route of the ligand

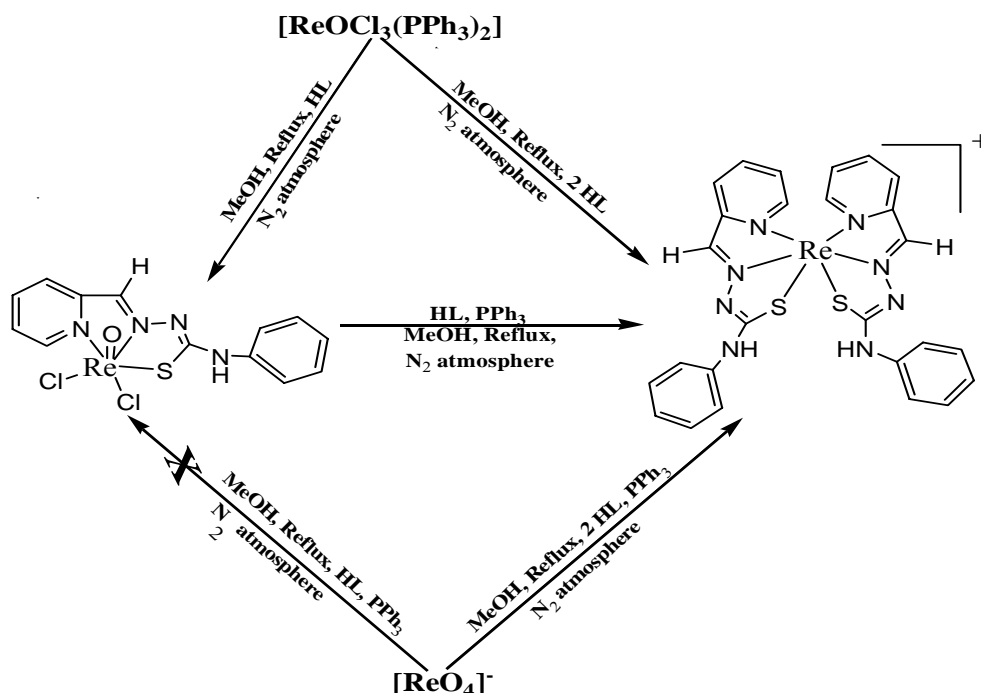
Synthesis of the complexes

New rhenium and zinc thiosemicarbazone complexes are synthesised. The reaction of [ReOCl₃(PPh₃)₂] with one equivalent of the tridentate ligand [HL] in MeOH at reflux and under nitrogen atmosphere gave the monomeric neutral complex [ReOCl₂(L)] as a red brick solid

(**Scheme2**). Reduction of Re(V)-oxo to Re(III) and the formation of the cationic [Re(L)₂]Cl complex as a black brown solid is observed, when an excess of [HL] is used and the reaction mixture is heated under reflux for a prolonged time. The reduction of the metal atom is most probably due to the liberated PPh₃. This has been observed previously for many

reactions starting from $[\text{ReOCl}_3(\text{PPh}_3)_2]$,^[15] including exchange reactions with ligands of the type $[\text{HL}^2]$ ^[7]. However, the nature of the incoming ligand is essential to control the composition and oxidation state of the metal atom in the products. Whereas exclusively rhenium(III) cations of the composition $[\text{Re}(\text{L})_2]^+$ and decomposition products could be isolated when acetylpyridine thiosemicarbazones $[\text{HL}^2]$ are used.^[8] The reaction with the corresponding 2-pyridineformamide derivatives $[\text{HL}^1]$ ^[8] or with 2-formylpyridine *N*(4)-phenylthiosemicarbazone can be performed stepwise (see **Scheme2**) and oxorhenium(V) intermediates can be isolated in reasonable yields. This behaviour demonstrated that, the nature of substituents on -N(2) and/or -N(4) of the thiosemicarbazones is crucial to stabilize metal atoms in higher oxidation states.^[16] Significantly in terms of the possible application for radiopharmaceuticals, the $[\text{Re}(\text{L})_2]^+$ complex was prepared directly from

perrhenate by the addition of HCl and PPh_3 as the reducing agent. Whilst the reaction of $[\text{Re}^{\text{VII}}\text{O}_4]^-$ with one equivalent of the tridentate ligand [HL] in MeOH at reflux and in the presence of PPh_3 and HCl gave intractable black solid (see **Scheme2**). On the other hand $[\text{ZnCl}_2(\text{HL})]$ was obtained as a neutral yellow solid from the reaction of ZnCl_2 with [HL] in MeOH at reflux and under nitrogen atmosphere. These complexes are stable in solution and in solid state. The molar conductance of the complexes $[\text{ReOCl}_2(\text{L})]$ and $[\text{ZnCl}_2(\text{HL})]$ in (DMSO) lies in the (15.3-12.5) $\text{S cm}^2 \text{ mole}^{-1}$ range, indicating their non-electrolytic nature. While the conductance of $[\text{Re}(\text{L})_2]\text{Cl}$ in (DMSO) is (51.3) $\text{S cm}^2 \text{ mole}^{-1}$, indicating its electrolytic nature with (1:1) ratio,^[17] (**Table3**). The analytical and physical data (**Table1**) and spectral data (**Tables 2, 3 and 4**) are compatible with the suggested structures (**Figure3**). The atom numbering for the complexes described is the same as that employed in the ligand synthesis (**Scheme1**).



Scheme (2) The synthesis route of rhenium complexes

Table (1) Analytical and physical data of the ligand and its complexes

| Compound | Colour | m.p ^o c | Yield% | Found, (calc.)% | | | | |
|--------------------------|------------|--------------------|--------|------------------|----------------|------------------|------------------|------------------|
| | | | | C | H | N | S | Cl |
| [HL] | White | 199 | 75 | (60.91) 60.50 | (4.72) 4.89 | (21.86) 21.90 | (12.55) 12.77 | ----- |
| [Re(L) ₂]Cl | Dark brown | 175 | 63 | (42.76) 43.19 | (2.76) 3.01 | (15.34) 14.97 | (8.78) 8.61 | (4.85) 4.73 |
| [ReOCl ₂ (L)] | Red brick | >300 | 58 | (29.60) 29.50 | (1.91) 1.65 | (10.62) 10.23 | (6.08) 5.89 | (13.44) 14.02 |
| [ZnCl ₂ (HL)] | Yellow | >300 | 82 | (39.87) 39.32 | (2.83) 2.40 | (14.31) 14.22 | (8.19) 8.20 | (18.11) 18.43 |

(Calc.) : Calculated

IR Spectra

The IR bands most useful of determining the thiosemicarbazones mode of coordination are shown in (Table2). The IR spectrum of [ReO(L)Cl₂] (Figure1-2) shows the $\nu(\text{C}=\text{N})$ band of the ligand at 1596 cm^{-1} undergoes small shifts to higher frequency and appear at

1600 cm^{-1} , indicating coordination of the imine nitrogen N-(2). The spectrum of the ligand shows the thioamide IV band, which at 870 cm^{-1} , and it shifts to higher energy and appears at 891 cm^{-1} on coordination of the ligand. The absence of (N₃-H) band at 3120 cm^{-1} , indicates the coordination of the ligand in thiol

form. The spectrum shows band at 979cm^{-1} characteristic of the $\nu(\text{Re}=\text{O})$ stretching,^[18] additional evidence for coordination of the imine nitrogen is the presence of $\nu(\text{M}-\text{N})$ band at 432cm^{-1} .^[19] The IR spectrum of the $[\text{Re}(\text{L})_2]^+$ complex (**Figure1-3**) demonstrates symmetric coordination of the two thiosemicarbazone ligands through the nitrogen atoms of pyridine, azomethine groups and sulfur atoms, similar to the Re(III) complex with anionic thiosemicarbazone ligand, for which X-ray analysis confirmed a distorted octahedral geometry. The spectrum shows no band related to the $\nu(\text{Re}=\text{O})$. Moreover the absence of $(\text{N}_{(3)}-\text{H})$ band at 3126cm^{-1} , indicates the coordination of the ligand in thiol form. The IR spectrum of $[\text{Zn}(\text{HL})\text{Cl}_2]$ (**Figure1-4**) shows the imine $\nu(\text{C}=\text{N})$ band of the ligand at 1596cm^{-1} shifts to higher frequency and appear at 1620cm^{-1} , indicating coordination of the imine nitrogen N-(2). This increase is due to weaker coordination to the central ion in comparison with rhenium.^[20] The band at 3126cm^{-1} was attributed to $\nu(\text{N}_{(3)}-\text{H})$ in the IR spectrum of the ligand is still exist in the complex spectrum, and appeared at 3197cm^{-1} indicating the

coordination of the ligand to Zn(II) ion in thion form.

Electronic Spectra

The (U.V-Vis) spectrum of the complex $[\text{ReOCl}_2(\text{L})]$ displayed absorption peaks at $(216\text{nm})(46296\text{cm}^{-1})$ ($\epsilon_{\text{max}} = 4420\text{molar}^{-1}\text{cm}^{-1}$) and a shoulder at $(338\text{nm})(29585\text{cm}^{-1})$ ($\epsilon_{\text{max}} = 390\text{molar}^{-1}\text{cm}^{-1}$) assigned for ligand field. The peak at $(420\text{nm})(23809\text{cm}^{-1})$ ($\epsilon_{\text{max}} = 225\text{molar}^{-1}\text{cm}^{-1}$) assigned to (d-d) transition type (${}^3\text{T}_{1g}(\text{p}) \rightarrow {}^3\text{T}_{1g}$). This result is in agreement with that reported for oxo-Re(V) with octahedral geometry.^[21, 22] $[\text{Re}(\text{L})_2]\text{Cl}$ complex exhibits four absorption peaks at $(215\text{nm})(46511\text{cm}^{-1})$ ($\epsilon_{\text{max}} = 4410\text{molar}^{-1}\text{cm}^{-1}$) assigned to ligand field. The peak at $(390\text{nm})(25641\text{cm}^{-1})$ ($\epsilon_{\text{max}} = 1570\text{molar}^{-1}\text{cm}^{-1}$) was assigned to charge transfer. Whilst the peaks at $(451\text{nm})(22172\text{cm}^{-1})$ ($\epsilon_{\text{max}} = 788\text{molar}^{-1}\text{cm}^{-1}$) and a broad peak at $(605\text{nm})(165281\text{cm}^{-1})$ ($\epsilon_{\text{max}} = 195\text{molar}^{-1}\text{cm}^{-1}$) were attributed to d-d transitions type (${}^1\text{T}_{2g} \rightarrow {}^1\text{A}_{2g}$) and (${}^1\text{T}_{2g} \rightarrow {}^1\text{T}_{1g}$) respectively. This result is in agreement with that reported for Re(III) complexes with a distorted octahedral geometry.^[23] The $[\text{ZnCl}_2(\text{HL})]$ complex shows three absorption peaks at (215nm)

(46511cm⁻¹) (ϵ_{\max} =4410 molar⁻¹cm⁻¹)
and (329nm)(30395cm⁻¹) (ϵ_{\max} =1844
molar⁻¹cm⁻¹) assigned to ligand field.
Since the metal ion of the complex

belong to d¹⁰ system, the peak at
(408nm) (24509cm⁻¹) (ϵ_{\max} =210 molar⁻¹
cm⁻¹) was assigned to charge transfer.

Table (2) I.R spectral data (wave number ν) cm⁻¹ of the ligand [HL] and it's complexes

| Compound | $\nu(\text{N}_{(4)}\text{-H})$ $\nu(\text{N-NH})$ | $\nu(\text{C-H})$ | $\nu(\text{C=N})$ imine | $\nu(\text{C=C})$ $\nu(\text{C=N})$ | $\nu(\text{N-N})$ | $\nu(\text{C-S})$ | $\nu(\text{M-N})$ | Additional peaks |
|--------------------------|--|-------------------|----------------------------|--|-------------------|-------------------|-------------------|---|
| [HL] | 3305(w) 3126 | 2947(w) | 1597(s) | 1550(sh) 1496(sh) | 995 | 870 | - | 756, 690 $\delta(\text{C-H})$ Out of plane |
| [Re(L) ₂]Cl | ---- 3166 | 3043, 2927 | 1600 | 1523 1458 | 1004 | 903 | 428(w) | 756, 690 $\delta(\text{C-H})$ Out of plane |
| [ReOCl ₂ (L)] | ---- 3262 | 3066, 2927 | 1596 | 1554 1492, 1458 | 1022 | 891 | 432(w) | 979 $\nu(\text{Re=O})$. 752, 690 $\delta(\text{C-H})$ Out of plane. |
| [ZnCl ₂ (HL)] | 3259 3197 | 3028 | 1612 | 1558 1492, 1446 | 1010 | 906 | 415(w) | 759, 694 $\delta(\text{C-H})$ Out of plane. |

Recorded as KBr: s: strong, m: medium, w: weak.

Table (3) Electronic spectral data and conductivity measurement of [HL] and its metal complexes

| Compound | λ nm | ν cm ⁻¹ | ϵ_{\max} (molar ⁻¹ . cm ⁻¹) | $\Lambda_M(\Omega^{-1}$ cm ² mol ⁻¹) | Ratio |
|--------------------------|--------------------------|----------------------------------|--|--|---------|
| [HL] | 211 328 391 | 47393 30407 25575 | 4410 1720 334 | | |
| [Re(L) ₂]Cl | 215 390 451 605 | 46511 25641 22172 16528 | 4420 1570 786 195 | 51.3 | (1:1) |
| [ReOCl ₂ (L)] | 216 338 420 | 46296 29585 23809 | 4420 390 270 | 15.8 | Neutral |
| [ZnCl ₂ (HL)] | 215 342 409 | 46511 30395 24509 | 4410 1844 210 | 12.5 | Neutral |

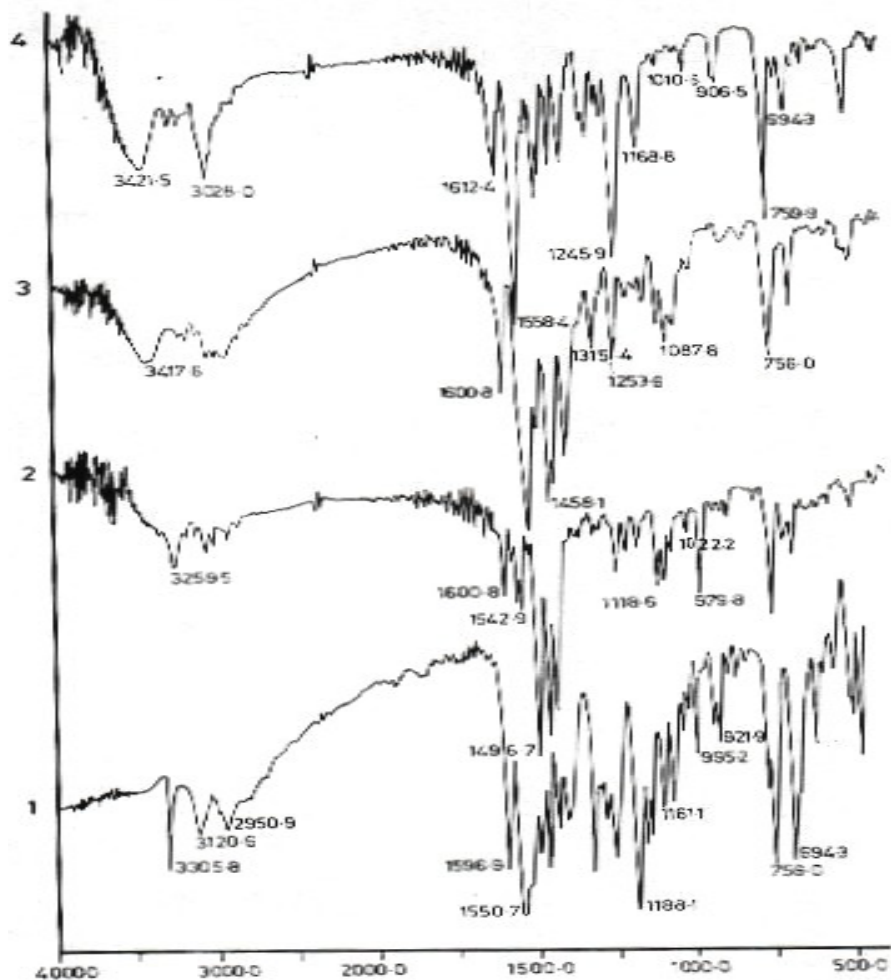


Figure 1 (IR) spectra (cm^{-1}) of:
 (1-1) The ligand [HL]
 (1-2) The complex $[\text{ReO}(\text{L})\text{Cl}_2]$
 (1-3) The complex $[\text{Re}(\text{L})_2\text{Cl}]$
 (1-4) The complex $[\text{Zn}(\text{HL})\text{Cl}_2]$

Mass Spectrum

The FAB(+) mass spectrum of $[\text{ReOCl}_2(\text{L})]$ showed peaks which could be assigned to a composition of $[\text{ReOCl}(\text{L})]^+$ at $m/z = 492$ ($M-\text{Cl}$)⁺. No evidence, however, was found for the molecular ion peak at $m/z = 528$ (M)⁺,

and the following fragments; $459 = (M-2\text{Cl})^+$, $467.9 = [M-\{\text{C}=\text{S}+\text{O}\}]^+$, $408.8 = [M-\{2\text{Cl}+(\text{C}=\text{S})+\text{O}\}]^+$, $354 = [M-\{\text{O}+(\text{N}-\text{N}-\text{C}=\text{S})\}]^+$, $153 = [M-\{\text{O}+(\text{N}-\text{N}-\text{C}=\text{S})+(\text{H}_2\text{C}=\text{CH}_2)\}]^+$ detected. The FAB(+) mass spectrum of $[\text{Re}(\text{L})_2]^+$ showed the following fragments ions

peak at $m/z= 587= [M-(Ph+S)]^+$, $560= [M-(Ph+HN-C=S)]^+$, $542= [M-(2Ph)]^+$, $250= [M-2(Ph+HN-C-NH-N=CH-py)]^+$.

NMR Studies

The Re(V), Re(III) and Zn(II) complexes are diamagnetic (**Table 4**). The ^1H and ^{13}C NMR spectra of Re(III) complex show well defined narrow lines which is unusual for what formally d^4 octahedral system and might show the nature of the delocalisation ligand. It was suggested that binding of the pyridine nitrogen to form a chelate may account for the diamagnetic nature of the complexes due to the π -system in which the lone pair of electrons is donated by pyridine nitrogen into the t_{2g} set of the metal.^[24] Similar mechanisms may be involved in the thiosemicarbazone system. The NMR spectrum of Re(III) complex is consistent with the symmetric nature of the complex. The ^{13}C NMR of the complex is shown in (**Figure2**) and exhibits 13 resonances. The signal for the C-S carbon comes around $\delta= 186.51$ ppm compared with $\delta= 176.34$ ppm in the free ligand which is consistent with thiolate type coordination to the rhenium rather than thion.^[8] The deprotonation of the ligand is confirmed in the ^1H NMR spectra of Re complex by the

absence of a resonance assigned to the hydrazinic proton which is readily detectable in the spectrum of the free ligand at $\delta=12.11$ ppm. The NMR spectra suggested the presence of the $[\text{Re}(\text{L})_2]\text{Cl}$ complex as a single species in solution. ^1H and ^{13}C NMR spectra of Re(V) complex showed well defined downfield lines in comparison with that for Re(III) and Zn(II) spectra. This can be attributed to the high oxidation state of the metal centre, which is formally d^2 system. The NMR spectra of Re(V)-oxo complex suggest the presence of two isomers in solution. The signal for the C-S carbon comes at about $\delta= 193.62$ ppm for isomer A and at 184.00 ppm for isomer B compared with $\delta= 176.34$ ppm in the free ligand and is consistent with thiolate like coordination to the rhenium(V) rather than thion. The deprotonation of the ligand is confirmed in the ^1H NMR spectrum of Re(V)-oxo complex by the absence of a resonance assigned to the hydrazinic proton which is readily detectable in the spectrum of the free ligand at $\delta=12.11$ ppm. In addition, the ^1H NMR spectrum of Re(V)-oxo complex shows resonances at chemical shift 10.80 and 10.68 ppm which were assigned to $\text{N}_{(4)}\text{-H}$ of

isomers A and B respectively. These signals are disappeared on addition of D_2O to the NMR solution supporting the presence of two isomers in solution. There are several possibilities for isomers of asymmetric tridentate ligands, one is the differing in the disposition of the $Re=O$ group. These are non-superimposable enantiomers, which might be observed in solution by NMR spectroscopy. There are also possible isomers involving different conformations of the backbone which should occur also for $Re(III)$ complex, but are not apparently observed. This observation suggests this is not the case. On the other hand the ^{13}C spectrum for $Zn(II)$ (**Figure2**), shows the signal for the C-S carbon at $\delta = 176.49$ ppm which is consistent with thion like coordination to the zinc. This has been confirmed by the 1H NMR spectrum of the presence of the hydrazinic proton at $\delta = 12.11$ ppm.

Table (4) ^1H , ^{13}C NMR Data for the ligand and its complexes measured in DMSO-d^6 and chemical shift in ppm (δ)

| Compound | Funct. Group | δ_s (p.p.m) ^b |
|--------------------------|---|--|
| [HL] | | |
| ^1H | -N-N ₍₂₎ -H ^a ; -N ₍₄₎ -H ^a ; -N=C-H; Ar- H; Ar- H Ar- H; Ar- H | 12.11 (1H, s, br.); 10.33 (1H, s); 8.67 (1H, s); 8.47(1H, s);8.23 (s, 1H) 8.11 (1H, s); 7.88-7.44(m, 6H) |
| ^{13}C | (C ₇ -S); (C ₆ =N); (C ₅); (C ₁); (C ₈); (C ₃); (C _{10,11}); (C _{9,13}); (C ₂); (C ₁₁); (C ₄). | 176.32; 153.04; 149.22; 142.97; 138.84; 136.35; 127.98; 125.87; 124.93; 124.10; 120.52. |
| [Re(L) ₂]Cl | | |
| ^1H | - N ₍₄₎ -H ^a ; -N=C-H;Ar- H Ar- H; Ar- H Ar- H; Ar- H; Ar- H; Ar- H. | 11.48 (1H, s); 8.48 (1H, s);8.34 (1H, d, J_{H-H} = 7.4 Hz) 7.88 (2H, d, J_{H-H} = 0.8 Hz) ;7.75 (1H, d, J_{H-H} = 9.76 Hz) 7.60 (1H, s); 7.39 (1H, s)7.22-7.15 (1H, m); 6.95 (1H, s) |
| ^{13}C | (C ₇ -S); (C ₆ =N); (C ₅); (C ₁); (C ₈); (C ₃); (C _{10,11}); (C _{9,13}); (C ₂); (C ₁₁); (C ₄). | 186.51; 159.40; 158.48; 140.78; 136.82; 133.09; 129.01; 127.99; 126.70; 123.78; 120.08. |
| [ReOCl ₂ (L)] | | |
| ^1H | | |
| Isomer A | - N ₍₄₎ -H ^a -N=C-H | 10.80 (1H, s) 9.03 (1H, s) |
| Isomer B | - N ₍₄₎ -H ^a -N=C-H | 10.68 (1H, s) 8.81 (1H, s) |
| ^{13}C | | |
| Isomer A | (C ₇ -S); (C ₆ =N); (C _{Ar}); (C _{Ar}); (C _{Ar}); (C _{Ar});(C _{Ar}); (C _{Ar}); (C _{Ar}); (C _{Ar}); (C _{Ar}). | 193.62; 161.13; 151.06; 141.23; 129.81; 129.00; 128.70; 128.40; 127.97; 124.82; 121.73. |
| Isomer B | (C ₇ -S); (C ₆ =N); (C _{Ar}); (C _{Ar}); (C _{Ar}); (C _{Ar}); (C _{Ar}); (C _{Ar});(C _{Ar}); (C _{Ar}); (C _{Ar}). | 184.00; 162.13; 154.91; 150.16; 143.12; 137.78; 129.28; 126.41; 125.99; 124.82; 123.59. |
| [ZnCl ₂ (HL)] | | |
| ^1H | -N-N ₍₂₎ -H ^a ; N ₍₄₎ -H ^a ; -N=C-H; Ar- H; Ar- H; Ar- H; Ar- H; Ar- H; Ar- H. | 12.11 (1H, s); 10.33 (1H, s); 8.63 (1H, s) 8.45 (1H, s); 8.21 (1H, s); 8.08 (1H, s); 7.58 (1H, s); 7.28 (2H, s); 7.11 (1H, s). |
| ^{13}C | (C ₇ -S); (C ₆ =N); (C ₅); (C ₁); (C ₈); (C ₃); (C _{10,11}); (C _{9,13}); (C ₂); (C ₁₁); (C ₄). | 176.49; 151.86; 148.04; 140.97; 139.01; 138.36; 128.19; 125.97; 125.03; 124.65; 121.64. |

^a disappears on D₂O exchange; ^b chemical shift from TMS.

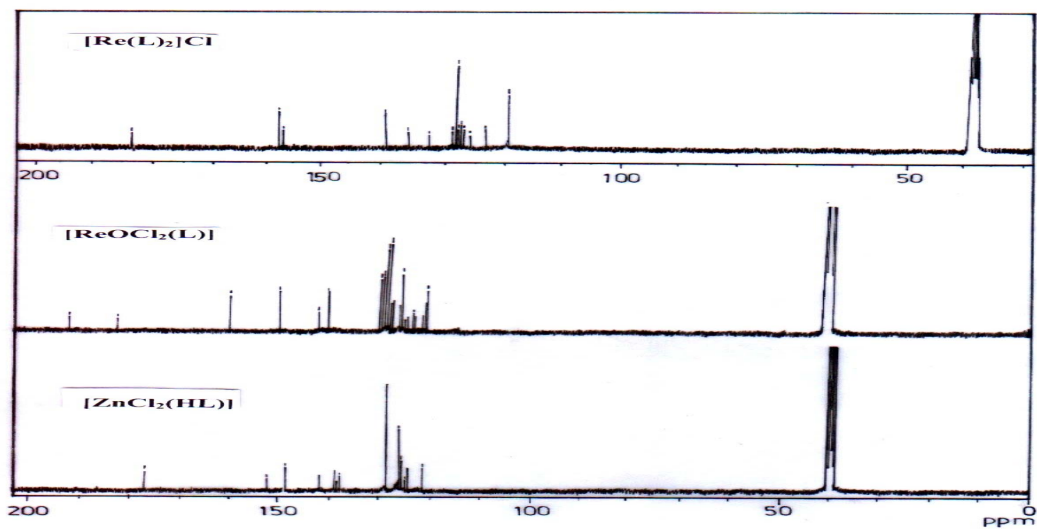
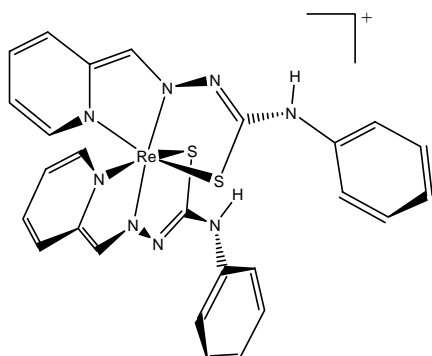
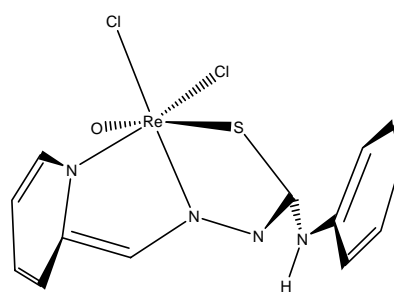


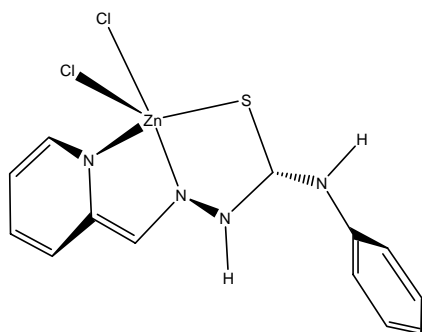
Figure 2 ^{13}C NMR spectra of the complexes (DMSO- d^6)



The proposed structure of $[\text{Re}(\text{L})_2]^+$



The proposed structure of $[\text{ReOCl}_2(\text{L})]$



The proposed structure of $[\text{ZnCl}_2(\text{HL})]$

Figure 3 The suggested structure of the complexes

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