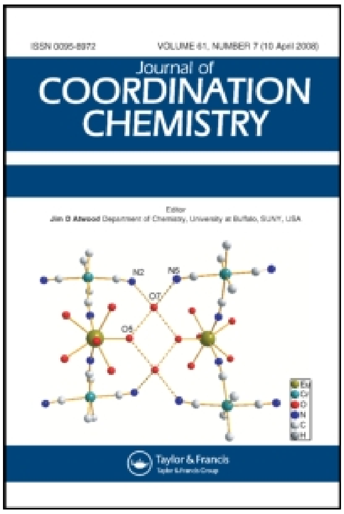

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SYNTHESIS AND THERMAL INVESTIGATIONS OF 2-HYDRAZINO-BENZIMIDAZOLE COMPLEXES OF RHENIUM(V) IN THE SOLID STATE

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SYNTHESIS AND THERMAL INVESTIGATIONS OF 2-HYDRAZINO-BENZIMIDAZOLE COMPLEXES OF RHENIUM(V) IN THE SOLID STATE

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A new series of rhenium(V) complexes was prepared by reaction of 2-hydrazinobenzimidazole (L), alone or mixed with KSCN, with $H_2[ReOCl_5]$. Mononuclear complexes of different types, $[ReOLCl(OH_2)_2]Cl_2 \cdot 2H_2O$, $[ReOL_2(OH_2)_3]Cl_3$, $[ReOLCl_3(OH_2)]$, $[ReOL(SCN)_2Cl(OH_2)] \cdot 2H_2O$ and $[ReOL(SCN)Cl_2(OH_2)]$, along with dinuclear complexes, $[Re_2O_3LCl_4(OH_2)_2] \cdot 2H_2O$ and $[Re_2O_3L_2Cl_2(OH_2)_4] \cdot Cl_2$, were obtained depending on the metal: ligand molar ratio and the concentration of hydrochloric acid containing the starting rhenium complex. These complexes decompose through several isolable, as well as non-isolable, intermediates during heating. $[Re_2O_3L_2Cl_4]$, $[ReOL_2Cl]$ and $[Re_2O_3L_2(SCN)_4]$, were synthesized pyrolytically in the solid state from the corresponding rhenium complexes. The electronic absorption spectra and magnetic moments prove octahedral configuration of the complexes.

Conductivity measurements, IR and ^1H NMR spectroscopy combined with thermal analyses, show that the ligand behaves as a neutral, mono- or bidentate ligand towards rhenium.

Keywords: Rhenium; benzimidazole; thermal analysis; pyrolysis

INTRODUCTION

Rhenium(V) complexes have recently been prepared and investigated by several authors.[1–4] Benzimidazole derivatives have antiinflammatory activity[5–9] and other biological activities[10–12] such as antibacterial, antiviral and anthelmintic. Thus the possibility exists of designing rhenium complexes with peculiar biological properties.

Organorhenium oxides and rhenium(V) oxo complexes with tetradentate Schiff bases were found to catalyze olefin oxidation.[1,13]

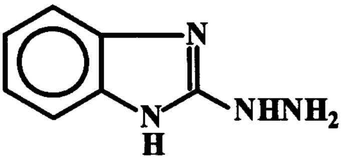


FIGURE 1 2-Hydrazinobenzimidazole, L.

We have previously synthesized rhenium(V) complexes with Lewis base ligands (O-, N- and/or S-donors).[14–17] As a continuation of our work, 2-hydrazinobenzimidazole (Figure 1) was used as a nitrogen donor ligand and mixed with KSCN to form different complexes with rhenium(V). The thiocyanate anion behaves as a unidentate monoanionic ligand through its sulfur atom and the ligand (L) behaves as a unidentate ligand, through the nitrogen atom of the terminal hydrazino group, or as a bridge, through the nitrogen atom of the terminal hydrazino group and the nitrogen atom of the C=N group inside the ring and/or as a neutral bidentate ligand with the same coordination sites as in the bridging case. The type of complex obtained depends on the molar ratio of the ligand : metal and the concentration of hydrochloric acid containing the starting metal complex.

The thermal investigation explored the possibility of obtaining some new rhenium(V) complexes pyrolytically in the solid state, which cannot be synthesized from solution.

The aim of the present study is to synthesize new rhenium(V) complexes, investigate the thermal decomposition behavior of these complexes, and isolate the possible intermediates formed upon heating.

EXPERIMENTAL

The starting rhenium complex, $H_2[ReOCl_5]$, and 2-hydrazinobenzimidazole were prepared by literature method.[18–20] KSCN was a BDH product. Ethanol, DMF, 1,4-dioxane, acetone, chloroform, ether, DMSO and HCl were reagent grade chemicals.

Preparation of the Rhenium Complexes

Complexes Prepared in 2 N HCl Solutions

As the starting Re(V) complex, $H_2[ReOCl_5]$, undergoes hydrolysis in HCl solutions below 6 N, the following preparations were accomplished by using this concentrated medium and subsequent dilution to 2 N by adding the ligand dissolved in the appropriate amount of water. It seems that the rate of formation of the new complexes, in these cases, is faster than hydrolysis of the starting Re(V) complex.

Molar Ratio M: L, 2:1

$[Re_2O_3(\mu\text{-}L)Cl_4(OH_2)_2]\cdot 2H_2O$ (I) Fifty mL of a 0.09 M $H_2[ReOCl_5]$ solution, *i.e.* containing 1.717 g (4.5 mmol) of the starting Re(V) compound in 6 N HCl, was added gradually to 0.333 g (2.25 mmol) of the ligand in 100 mL distilled water. The mixture was stirred for 6 h and then kept at room temperature for two days. The resulting precipitate was filtered, washed with 2 N HCl, chloroform and finally with ether.

Molar Ratio M: L, 1:2

$[Re_2O_3L_2Cl_2(OH_2)_4]\cdot Cl_2$ (II) This compound was prepared similar to **I** except that the amount of ligand was 1.332 g (9.0 mmol).

Complexes (I) and (II) were soluble in DMF, DMSO and partially soluble in ethanol but insoluble in 1,4-dioxane.

Complexes Prepared in 6 N HCl Solutions

Molar Ratio M: L, 2:1

$[ReOLCl(OH_2)_2]Cl_2\cdot 2H_2O$ (III) Fifty mL of a 0.09 M $H_2[ReOCl_5]$ solution containing 1.717 g (4.5 mmol) of the starting Re(V) compound in 6 N HCl was added gradually to 0.333 g (2.25 mmol) of the ligand and the mixture was stirred at room temperature for 7 h, then stored for two days at the same temperature. The resulting precipitate was filtered, washed with 6 N HCl, chloroform and finally with ether.

Molar Ratio M: L, 1:1

$[ReOL_2(OH_2)_3]Cl_3$ (IV) This compound was prepared similar to the previous complex except that the amount of ligand was doubled.

Molar Ratio M: L: SCN$^-$, 1:1:1

$[ReOL(SCN)_2Cl(OH_2)]\cdot 2H_2O$ (VI) Fifty mL of a 0.09 M $H_2[ReOCl_5]$ solution, *i.e.* containing 1.717 g (4.5 mmol) of the starting Re(V) compound in 6 N HCl, was added gradually to a mixture of 0.666 g (4.5 mmol) of 2-hydrazinobenzimidazole and 0.436 g (4.5 mmol) of KSCN. The mixture was stirred for 7 h, then kept at room temperature for two days. The resulting precipitate was filtered, washed with 6 N HCl, chloroform and then ether. Complexes **III**, **IV** and **VI** were soluble in DMF, DMSO and insoluble in 1,4-dioxane. Complex **VI** was soluble in ethanol but complexes **III** and **IV** were only partially soluble in ethanol.

Complexes Prepared in 9 N HCl Solution

Molar Ratio M : L, 2 : 1

$[ReOLCl_3(OH_2)]$ (**V**) Hundred mL of 0.045 M (4.5 mmol) of $H_2[ReOCl_5]$ in 9 N HCl was added gradually to 0.333 g (2.25 mmol) of 2-hydrazinobenzimidazole, and the mixture was stirred at room temperature for the resulting 8 h, then kept for two days at the same temperature. The resulting precipitate was filtered, washed with 9 N HCl, chloroform and finally with ether.

Molar Ratio M : L : SCN⁻, 1 : 1 : 1

$[ReOL(SCN)Cl_2(OH_2)]$ (**VII**) Hundred mL of 0.045 M (4.5 mmol) $H_2[ReOCl_5]$ in 9 N HCl was added gradually to a mixture of 0.666 g (4.5 mmol) of 2-hydrazinobenzimidazole and 0.436 g (4.5 mmol) of KSCN. The mixture was stirred for 8 h and then kept at room temperature for two days. The resulting precipitate was filtered, washed with 9 N HCl, chloroform and then ether. Complexes **V** and **VII** were soluble in DMF, DMSO and ethanol, but insoluble in 1,4-dioxane.

Physical Measurements and Analyses

Electronic spectra of solutions of the complexes in DMF were recorded on a JASCO model V-550 UV-vis Spectrophotometer. IR spectra were recorded on a Perkin-Elmer 598 Spectrometer using KBr discs, polystyrene was used as a calibrant. Far-IR spectra were measured with a Nicolet 20F-FTIR spectrometer using polyethylene discs. Magnetic moments were measured by the Gouy method at room temperature using a Johnson Matthey Alfa, Model No. MKI, magnetic susceptibility balance with $Hg[Co(CNS)_4]$ as a calibrant. Diamagnetic corrections were calculated from Pascal's constants.[21] ^1H NMR spectra (DMSO-d_6) were recorded at room temperature on a cryomagnet for NMR spectroscopy 200 MHz/52 MM, a product of Spectrospin and Bruker using TMS as an internal standard. TG-DTA measurements were carried out on a Perkin-Elmer high temperature differential thermal analyzer with 3700 data point resolution. Conductivities were measured in solutions of the complexes in DMF (10^{-3} M) using a Wissenschaftlich-Technische Werkstätten, D 8120 Weilheim, Germany, Model LBR 40 A, conductivity meter. Microanalyses for carbon, hydrogen, nitrogen and sulfur were carried out at the Microanalytical center, Cairo University, Giza, Egypt.

Rhenium and chlorine were determined gravimetrically as nitron perrhenate and silver chloride, respectively.[22]

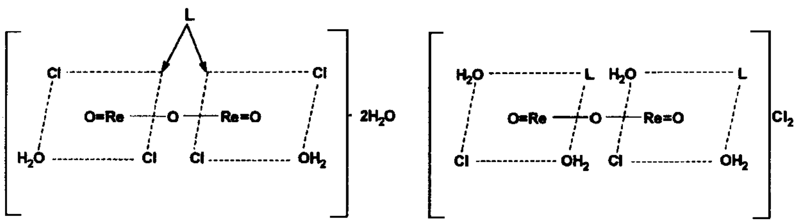
RESULTS AND DISCUSSION

The reactions of $H_2[ReOCl_5]$ with 2-hydrazinobenzimidazole as a ligand at different concentrations of hydrochloric acid solutions and at room temperature yielded different products. Mononuclear rhenium(V) complexes were obtained in 6 N HCl solutions with molar ratios of 2 : 1 and 1 : 1 (M : L) or in 9 N HCl solution with a molar ratio of 2 : 1 (M : L), Figure 2 (structures **III**, **IV** and **V**). Dinuclear rhenium(V) complexes were obtained in 2 N HCl solutions and molar ratios of 2 : 1 and 1 : 2 (M : L), Figure 2 (structures **I** and **II**). The reaction of a 1 : 1 mixture of KSCN and 2-hydrazinobenzimidazole, (L), with $H_2[ReOCl_5]$ in 6 N HCl yielded different products of mononuclear rhenium(V) complexes, Figure 2 (structures **VI** and **VII**).

The isolated rhenium(V) complexes were amorphous upon removal of the solvent. Tables I–V show the results obtained.

IR Spectra

The IR spectra of the free ligand (L) and its complexes are listed in Table II. The IR spectrum of the free ligand (L) shows three bands of νNH_2, νNH



I II

FIGURE 2(a)

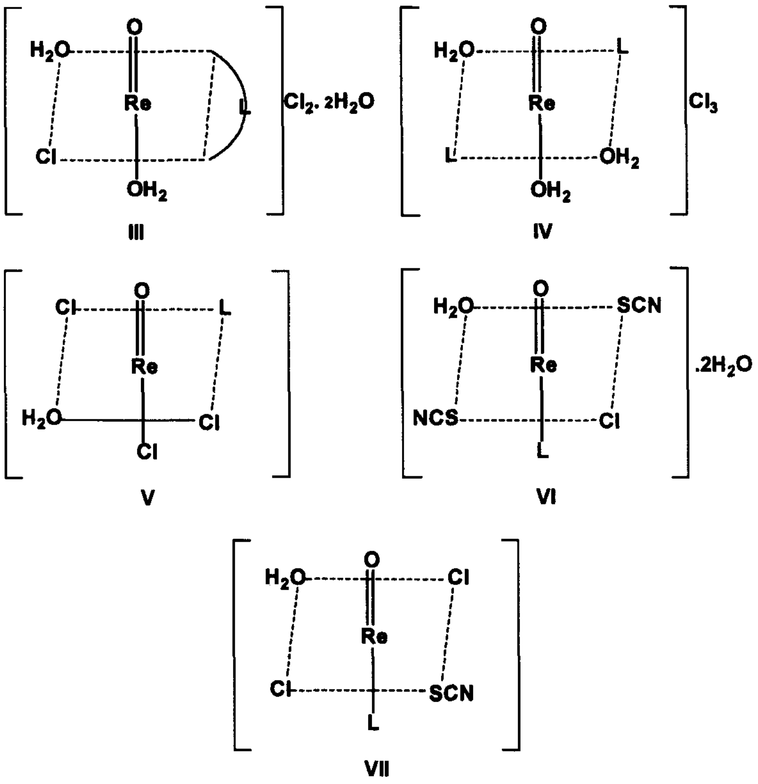


FIGURE 2(b)

FIGURE 2 Structures of mono- and dinuclear rhenium(V) complexes. A: Dinuclear rhenium(V) complexes. I – Tetrachloro-μ-oxo-diaquo(μ-2-hydrazinobenzimidazole)dioxodirhenium(V) dihydrate complex. II – Dichloro-μ-oxo-tetraaquo(di-2-hydrazinobenzimidazole)dioxodirhenium(V) chloride complex. B: Mononuclear rhenium(V) complexes. III – Chlorodiaquo(2-hydrazinobenzimidazole)oxorhenium(V) chloride dihydrate complex. IV – Triaquo(di-2-hydrazinobenzimidazole)oxorhenium(V) chloride complex. V – Trichloroaquo-(2-hydrazinobenzimidazole)oxorhenium(V) complex. VI – Chlorodithiocyanatoaquo(2-hydrazinobenzimidazole)oxorhenium(V) dihydrate complex. VII – Dichlorothiocyanatoaquo-(2-hydrazinobenzimidazole)oxorhenium(V) complex.

(side chain) and νNH (ring) at 3220, 3170 and 3135 cm^{-1}. The first band is assigned to the ν_{asymm} NH_2 while the second band is assigned to the overlap of ν_{sym} NH_2 and νNH of the side chain. The third band is assigned to νNH of the heterocyclic ring. In all complexes, ν_{asymm} of the NH_2 group was shifted (30–40 cm^{-1}) to lower frequencies, due to coordination of the NH_2 group. The other stretching vibrations of the NH (side chain) and NH (ring) were not significantly affected, indicating that the nitrogen atoms of these

TABLE I Elemental Analyses of Rhenium(V) Complexes

	Compound	*Color*	*Yield* (%)	*Elemental analyses* (Found/calcd.)					
				% C	% H	% N	% S	% Re	% Cl
I	$[Re_2O_3(\mu\text{-}L)Cl_4(OH_2)_2]\cdot 2H_2O$	Deep brown	72	10.60	1.96	6.90	—	47.70	18.30
	$C_7H_{16}N_4O_7Re_2Cl_4$			(10.73)	(2.04)	(7.16)	—	(47.60)	(18.15)
II	$[Re_2O_3L_2Cl_2(OH_2)_4]\cdot Cl_2$	Gray	63	17.80	2.40	11.90	—	39.80	15.30
	$C_{14}H_{24}N_8O_7Re_2Cl_4$			(18.05)	(2.85)	(12.04)	—	(40.03)	(15.26)
III	$[ReOLCl(OH_2)_2]Cl_2\cdot 2H_2O$	Deep green	68	15.80	3.00	10.30	—	35.15	20.20
	$C_7H_{16}N_4O_5ReCl_3$			(15.89)	(3.03)	(10.59)	—	(35.22)	(20.14)
IV	$[ReOL_2(OH_2)_3]Cl_3$	Blue	70	25.40	3.30	16.85	—	28.20	16.10
	$C_{14}H_{22}N_8O_4ReCl_3$			(25.50)	(3.34)	(17.00)	—	(28.27)	(16.17)
V	$[ReOLCl_3(OH_2)]$	Deep blue	58	17.50	2.20	11.60	—	39.25	22.70
	$C_7H_{10}N_4O_2ReCl_3$			(17.69)	(2.10)	(11.79)	—	(39.22)	(22.43)
VI	$[ReOL(SCN)_2Cl(OH_2)]\cdot 2H_2O$	Pale brown	65	19.40	2.40	15.00	11.60	33.60	6.20
	$C_9H_{14}N_6S_2O_4ReCl$			(19.43)	(2.52)	(15.11)	(11.52)	(33.51)	(6.39)
VII	$[ReOL(SCN)Cl_2(OH_2)]$	Brownish-red	60	19.40	2.10	14.00	6.40	37.40	14.35
	$C_8H_{10}N_5SO_2ReCl_2$			(19.31)	(2.01)	(14.08)	(6.43)	(37.45)	(14.28)

TABLE II Characteristic IR Bands (cm^{-1})[a] of 2-hydrazinobenzimidazole and Its Rhenium(V) Complexes

Compound	ν_{asymm} NH_2	ν_{sym} $NH_2 + \nu NH$ (*side chain*)	νNH (*ring*)	νSCN	δNH_2	$\nu C{=}N$	$\nu Re{=}O$	$\nu Re{-}N$	$\nu Re{-}Cl$	$\nu Re{-}S$	γCH[b]	*Additional bands*
$C_7H_8N_4$	3220 m	3170 m	3135 w	—	1635 m	1520 s	—	—	—	—	740 s	—
I	3190 w	3165 w	3130 w	—	1610 m	1492 m	905 s	460 m, 435 w	355 m, 338 w	—	740 s	3530 br (coordinated water), 3380 br (lattice water), 632 m, 615 w ν(Re–O), 712 m, ν_{asymm} (Re–O–Re)
II	3184 m	3168 w	3132 w	—	1620 s	1505 s	907 s	465 m	357 m	—	743 s	3490 br (coordinated water), 640 w, 612 m ν(Re–O), 708 m, ν_{asymm} (Re–O–Re)
III	3188 m	3163 w	3130 w	—	1625 s	1490 s	992 s	458 m, 427 w	362 m	—	740 s	3510 br (coordinated water), 3365 br (lattice water), 650 m ν(Re–O)
IV	3180 m	3165 w	3135 w	—	1622 s	1512 s	996 s	462 s	—	—	745 s	3480 br (coordinated water), 672 m, 627 w ν(Re–O)
V	3182 m	3164 w	3132 w	—	1624 s	1510 s	1002 s	465 m	357 m, 332 w	—	745 s	3470 br (coordinated water), 675 m ν(Re–O)
VI	3185 m	3167 w	3136 w	2058 s	1623 s	1509 s	997 s	466 m	352 m	305 w, 290 w	743 s	3460 br (coordinated water), 3350 br (lattice water), 677 m ν(Re–O)
VII	3180 m	3164 w	3135 w	2050 s	1623 s	1508 s	999 s	465 m	355 m, 332 m	293 w	740 s	3485 br (coordinated water), 674 m ν(Re–O)

[a] s = strong, m = medium, w = weak and br = broad.

[b] γ(CH) of the four adjacent hydrogen atoms of phenyl ring.

groups are not involved in coordination to the metal. On the other hand, νC=N was shifted to lower frequency (28–30 cm^{-1}) for complexes **I** and **III**, indicating that the nitrogen of the C=N group is involved in complexation. Thus, in these complexes the ligand is a neutral, bidentate donor, through the nitrogen atoms of the terminal NH_2 group and the C=N group of the ring.

The participation of the nitrogen atom(s) of the terminal NH_2 group and/or C=N group was also confirmed by the appearance of new bands at 427–466 cm^{-1} attributed to νRe–N.[23] The νRe=O band occurs at 992–1002 cm^{-1}, for the mononuclear complexes and at 905–907 cm^{-1} for the dinuclear complexes, consistent with values cited in the literature for similar mono- and dinuclear complexes.[16,17,24,25]

The IR spectra of the dinuclear rhenium(V) complexes, structures **I** and **II** in Figure 2, show new bands assigned to νRe–Cl at 355 and 338 cm^{-1} for the former complex and at 357 cm^{-1} for the latter, indicating coordination of chloride ions to the central rhenium(V) cation.[24] In addition, a new band appears at 712 and 708 cm^{-1} for complexes **I** and **II**, respectively, indicating that the bridging oxygen atom in these complexes links the two rhenium(V) cations (Re–O–Re).[26]

The stretching vibrations of coordinated water molecules appear at 3530 and 3490 cm^{-1} for complexes **I** and **II**, respectively. Two new bands also appear in the region 612–640 cm^{-1} for complexes **I** and **II**, where trans-coordinated water molecules are present and are due to ν_{asymm} and ν_{sym} of the Re–O linkage.[16] Also, complex **I** shows a broad band at 3380 cm^{-1} due to H-bonded lattice water molecules.

The mononuclear complexes, structures **III**, **IV** and **V** in Figure 2, show new bands due to νRe–Cl at 362 cm^{-1} for complex **III** and at 357 and 332 cm^{-1} for complex **V**, while complex **IV** does not show any bands in this region, indicating that the chloride ions are not present in the inner sphere of the latter complex. The stretching vibrations of coordinated water molecules appear at 3510, 3480 and 3470 cm^{-1} for complexes **III**, **IV** and **V**, respectively. The bands due to rhenium–oxygen bonds of coordinated water molecules were observed in the range 627–675 cm^{-1}.

The IR spectrum of mononuclear complexes **VI** and **VII** in Figure 2 showed a new strong band at 2058 cm^{-1} for the former and at 2050 cm^{-1} for the latter, which indicates coordination of SCN^- via the sulfur atom.[17,27] The Re–S stretching frequencies appear at lower frequencies, 290–305 cm^{-1}. New bands also appear in the region 332–355 cm^{-1} for νRe–Cl. The stretching vibrations of coordinated water molecules appear at 3460 and 3485 cm^{-1}; in addition, new bands are seen at 677 and 674 cm^{-1} due to νRe–O. Also, complex **VI** shows a broad band at 3350 cm^{-1} due to H-bonded lattice water molecules.

UV Visible Spectra

The UV spectrum of the free ligand shows two absorption bands at 263 and 311 nm. The visible spectrum of the starting rhenium complex (d^2) shows a main band at 780 nm. The prepared rhenium complexes show three bands at 256–262, 336–354, and 416–429 nm. The blue-shift of the visible bands in these complexes indicates the replacement of chloride ions by ligand molecules. The transition in the visible region may be assigned to $d\pi(\mathrm{Re}) \rightarrow \pi^*(\mathrm{L})$ transition and the UV region is assigned to intraligand $\pi \rightarrow \pi^*$ transitions.[28]

Magnetic Moments

The oxo complexes of rhenium(V) are all diamagnetic.[29] The magnetic moments of rhenium(V) complexes, Table III, confirm their diamagnetic character.

Conductivity Measurements

Conductivity measurements, Table III, prove that complexes **I**, **V**, **VI** and **VII** are non-electrolytes while complexes **II**, **III** and **IV** are 1 : 2, 1 : 2 and 1 : 3 electrolytes, respectively.

TABLE III Physico-chemical Measurements of the Starting Re(V) Complex, 2-hydrazinobenzimidazole and Its Rhenium(V) Complexes

Compound	*Molar conductance*[a] (ohm^{-1} cm^2 mol^{-1})	μ_{eff}[b] (B.M.)	$\lambda_{\max}$[a] (nm)
$C_7H_8N_4$	—	—	263, 311
$H_2[ReOCl_5]$[c]	—	—	420, 480, 780
I	14.0	0.08	258, 340, 425
II	92.0	0.12	259, 337, 422
III	89.0	0.15	258, 336, 429
IV	138.0	0.07	256, 348, 427
V	7.6	0.04	258, 352, 428
VI	7.1	0.13	261, 348, 418
VII	9.8	0.14	262, 354, 416

[a] DMF solutions, 1×10^{-3} M, at 30°C.
[b] Measurements were performed at 27°C.
[c] A solution of the starting complex in 6 N HCl was used.

TABLE IV ^{1}H NMR of 2-hydrazinobenzimidazole and The Rhenium Complexes

Compound	δNH[a] (*ring*)	δNH (*side chain*)	δNH_2
$C_7H_8N_4$ (L)	12.86 (1H)	12.10 (1H)	9.60 (2H)
I	12.87 (1H)	12.37 (1H)	11.35 (2H)
II	12.94 (2H)	12.16 (2H)	11.23 (4H)
III	12.88 (1H)	12.45 (1H)	11.42 (2H)
IV	12.92 (2H)	12.25 (2H)	11.48 (4H)
V	12.87 (1H)	12.28 (1H)	11.30 (2H)
VI	12.92 (1H)	12.38 (1H)	11.57 (1H)
VII	12.95 (1H)	12.23 (1H)	11.46 (1H)

[a] Chemical shifts with reference to TMS.

Nuclear Magnetic Resonance Spectral Studies

The assignment of the main signals in the ^{1}H NMR spectra of 2-hydrazinobenzimidazole and its rhenium(V) complexes are listed in Table IV. The free ligand 2-hydrazinobenzimidazole showed signals at δ 12.86 ppm (1H) of the NH (ring), δ 12.10 ppm (1H) of NH (side chain) and δ 9.60 (2H) of the terminal NH_2 group.

In the complexes (**I–VII**), the signal corresponding to the NH_2 group is shifted downfield (11.23–11.57) due to a strong deshielding interaction by the metal cation. The signals corresponding to NH (ring) and NH (side chain) are slightly shifted downfield or not changed from the free ligand.

From the ^{1}H NMR and IR spectra, we suggest that the mode of coordination of ligand (L) is through the nitrogen atom of terminal NH_2 group when it acts as a neutral monodentate ligand and the nitrogen atoms of the terminal NH_2 group and the C=N group of the ring, when it acts as neutral bidentate ligand.

Thermal Analyses

Thermal analyses of the complexes, Table V, show that complexes **I**, **III** and **VI** became anhydrous at 97°C, 94°C and 105°C, respectively, due to elimination of lattice water which was accompanied by an endothermic peak. Further heating of the complexes leads to elimination of coordinated water molecule(s) at 170°C, 140°C, 148°C, 145°C and 147°C for complexes **I**, **II**, **IV**, **V** and **VII**, respectively. The removal of coordinated water molecule(s) from these complexes lead to non-isolable complex species, except for complex **II**. In complexes **III** and **VI**, elimination of coordinated water was accompanied by loss of HCl at 185°C and 245°C, respectively. The elimination of coordinated water from complexes **I**, **II**, **IV**, **V** and **VII** is accompained by an endothermic peak. Also, HCl molecules were eliminated

TABLE V Thermal Analysis of Rhenium(V) Complexes

Compound	*Temperature range* °C	*% Loss in weight Actual (Calc.)*	*DTA peak* °C		*Composition of the residue*	*Probable composition of expelled groups*
			Endo.	*Exo.*		
I	50–97	4.52 (4.60)	94	—	$[Re_2O_3LCl_4(OH_2)_2]$	Two molecules of lattice water
	97–170	8.90 (9.20)	153	—	$(Re_2O_3LCl_4]$	Two molecules of coordinated water
	170–340	13.75 (13.86)	325	—	$[Re_2O_3LCl_3]$	One molecule of HCl
II	85–140	7.80 (7.74)	135	—	$[Re_2O_3L_2Cl_4]$	Four molecules of coordinated water
	140–260	15.70 (15.58)	240	—	$[Re_2O_3L_2Cl_2]$	Two molecules of HCl
III	50–94	6.90 (6.81)	85	—	$[ReOLCl(OH_2)_2]Cl_2$	Two molecules of lattice water
	94–185	19.10 (18.82)	—	170	$[Re_2O_3L_2Cl_4]$	Two molecules of HCl and three molecules of water out of two complex molecules
IV	80–148	7.95 (8.20)	145	—	$[ReOL_2Cl_3]$	Three molecules of coordinated water
	148–305	19.00 (19.28)	300	—	$[ReOL_2Cl]$	Two molecules of HCl
V	85–145	3.90 (3.79)	135	—	$[ReOLCl_3]$	One molecule of coordinated water
	145–210	11.60 (11.78)	—	200	$[Re_2O_2L_2Cl_4]$	Two molecules of HCl out of two complex molecules
VI	50–105	6.50 (6.48)	95	—	$[ReOL(SCN)_2Cl(OH_2)]$	Two molecules of lattice water
	105–245	16.10 (15.23)	—	240	$[Re_2O_3L_2(SCN)_4]$	Two molecules of HCl and one molecule of water out of two complex molecules
VII	90–147	3.70 (3.62)	135	—	$[ReOL(SCN)Cl_2]$	One molecule of coordinated water
	147–245	11.40 (11.23)	—	230	$[Re_2O_2L_2(SCN)_2Cl_2]$	Two molecules of HCl out of two complex molecules

at higher temperatures, *i.e.* 340°C, 260°C, 305°C, 210°C and 245°C for complexes **I**, **II**, **IV**, **V** and **VII**, respectively. HCl molecules were eliminated from a chloride ion and a proton dissociated from the NH group of the ring of 2-hydrazinobenzimidazole, thus making the ligand anionic. The products of heating these complexes at the indicated temperatures are non-isolable, except for complex **IV**, which gave a stable species to be discussed later.

Pyrolytic Preparations of Some Rhenium(V) Complexes and their Characterization

New rhenium(V) complexes were prepared pyrolytically from the mother complexes **II**, **III**, **IV** and **VI**. Structures of the obtained products are discussed on the basis of their IR spectra, conductivity measurements and elemental analyses for rhenium, chlorine and sulfur.

$[Re_2O_3L_2Cl_4]$ was prepared by heating complex **II** at 140°C and complex **III**, at 190°C to constant weight. The color of the complex was pale brown and differed from the colors of both mother complexes. Its IR spectrum showed bands assigned to νRe=O at 907 cm^{-1} and νRe–O–Re at 708 cm^{-1}, which confirm that the complex is a dimer.[19,26] Also, it showed bands at 456 and 430 cm^{-1}, due to νRe–N, and at 359 and 335 cm^{-1}, due to νRe–Cl. The νC=N band was observed at 1495 cm^{-1}, indicating coordination of the nitrogen atom of the C=N group of the ring in addition to the nitrogen atom of the terminal amino group. Conductivity measurements in DMF proved that it is a non-electrolyte. From the previous results and the elemental analyses of rhenium and chlorine, the product obtained on heating can be represented as $[Re_2O_3L_2Cl_4]$ and its proposed structure is in Figure 3.

$[ReOL_2Cl]$ was prepared by heating complex **IV** at 310°C to constant weight; the color changed from blue to green. Its IR spectrum showed a band assigned to νRe=O at 994 cm^{-1}, which indicates the complex is

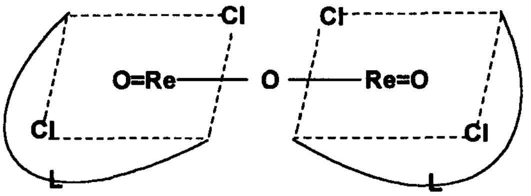


FIGURE 3 Structure of $[Re_2O_3L_2Cl_4]$, Tetrachloro-μ-oxo-bis(2-hydrazinobenzimidazole)-dioxodirhenium(V) complex, obtained by heating complex **II** to 140°C and complex **III** to 190°C.

mononuclear.[26] Bands due to νNH (ring) and νRe–O of the coordinated water molecules disappeared, while two new bands due to νRe–N were observed at 485 and 472 cm^{-1}. This indicates that the ligand (L) acts as a bidentate monoanion through the nitrogen of the amino group and the nitrogen of the NH group (ring). Conductivity measurements in DMF solution showed that it is a non-electrolyte. From the previous results and the elemental analyses of rhenium and chlorine, this product can be represented as [$ReOL_2Cl$] and its proposed structure is in Figure 4.

[$ReO_3L_2(SCN)_4$] was prepared by heating complex **VI** at 250°C to constant weight; the color changed from pale brown to reddish-brown. The IR spectrum of the heated product showed a new band at 713 cm^{-1} due to νRe–O–Re formed through dimerization. The stretching frequency of the Re=O bond was shifted to lower frequency, 912 cm^{-1}, additional evidence for dimerization of this complex on heating. Two new bands assigned to νRe–N appeared at 453 and 429 cm^{-1}. The bands corresponding to νSCN appear at $\approx$2050 cm^{-1}, indicating that the thiocyanate anion is still coordinated via sulfur. The conductance of a DMF solution of this product proves that it is a non-electrolyte.

From the previous results and the elemental analyses of rhenium and sulfur, this product can be represented as [$Re_2O_3L_2(SCN)_4$] and its structure is proposed in Figure 5.

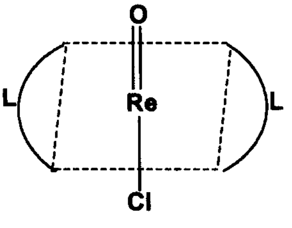


FIGURE 4 Structure of [$ReOL_2Cl$], Chloro-bis(2-hydrazinobenzimidazole)oxorhenium(V) complex, obtained by heating complex **IV** to 310°C.

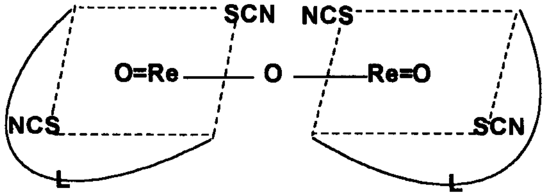


FIGURE 5 Structure of [$Re_2O_3L_2(SCN)_4$], Tetrathiocyanato-μ-oxo-bis(2-hydrazinobenzimidazole)dioxodirhenium(V) complex, obtained by heating complex **VI** to 250°C.

In all the proposed structures the *trans* configuration is shown since it is most stable.[2,30]

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