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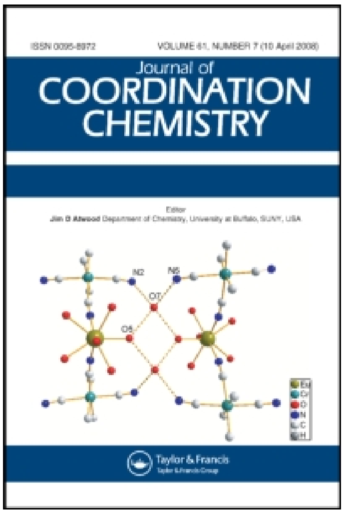

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Synthesis and Pyrolytical Studies of New Oxorhenium(V) Complexes with a Tetraaza Macrocyclic Ligand

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SYNTHESIS AND PYROLYTICAL STUDIES OF NEW OXORHENIUM(V) COMPLEXES WITH A TETRAAZA MACROCYCLIC LIGAND

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5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene (N_4L) reacts with the starting oxorhenium(V) complex, $H_2[ReOCl_5]$, to yield either mononuclear $[ReO(N_4L)(OH_2)]Cl_3$, or dinuclear $[Re_2O_3(N_4L)_2]Cl_4 \cdot 2H_2O$ depending on the concentration of hydrochloric acid in rhenium complex. The reaction of (N_4L) mixed with KSCN or PPh_3 with the oxorhenium(V) complex in 6 N HCl, yielded the mononuclear complexes $[ReO(N_4L)(SCN)]Cl_2 \cdot H_2O$ and $[ReO(N_4L)(PPh_3)]Cl_3 \cdot H_2O$ respectively. Both complexes have an octahedral configuration. These complexes decompose through several isolable, as well as non-isolable, intermediates during heating. $[Re_2O_3(N_4L^{\backslash})_2]$ ($N_4L^{\backslash}$ = dianionic tetradentate ions), $[ReO(N_4L)Cl]Cl_2$ and $[ReO(N_4L^{\backslash})(SCN)]$, were synthesized pyrolytically in the solid state from the corresponding rhenium(V) complexes. All have octahedral configurations. The ligand (N_4L) behaves in these complexes either as a neutral tetradentate or dianionic tetradentate ligand towards the oxorhenium ions. All complexes and the corresponding thermal products were isolated and their structures were elucidated by elemental analyses, conductance, IR and electronic absorption spectra, magnetic moments, ^{1}H NMR and TG-DSC measurements as well as by mass spectroscopy.

Keywords: Rhenium; Macrocycle; Tetraaza; Pyrolysis

INTRODUCTION

Rhenium(V) complexes derived from 1,1-hydroxyethylidene diphosphonate have been used for the palliative of metastatic bone pain [1]. $[^{186}Re/^{188}ReO(MAG_3)]^{2-}$ (MAG_3 = pentaanionic form of mercaptoacetyltriglycine in which the mercapto, amide and carboxyl groups are deprotonated) has been conjugated with antibodies and investigated for the detection and therapy of cancer [2,3].

The oxorhenium(V) complexes of diaminonucleoside and diaminoaldopentafuranoses are excellent competitive inhibitors of a purine specific RNase [4]. The rhenium(V) complexes containing phosphine ligands were employed for the photochemically-induced fixation and reduction of dinitrogen [5].

The potential of synthetic tetraaza macrocyclic complexes as models for more complex natural systems is well recognized [6]. In these macrocyclic complexes, both the metal ion and the size of the ring play an important role. Lindoy and coworkers [7,8] have reported a series of studies on the selective complexation of transition metal ions by polydentate ligands.

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The aza crownethers have complexation properties that are intermediate between those of all-oxygen crowns and of all-nitrogen cyclams. In most of the polyamide macrocyclic complexes, the amide nitrogen is coordinated and not the oxygen [9,10].

Herein, we report the synthesis and characterization of a diamidediimine macrocycle and its coordinating behavior with rhenium(V). The thermal studies explored the possibility of synthesizing new rhenium(V) complexes which cannot be synthesized from solution, pyrolytically in the solid state.

EXPERIMENTAL

The starting rhenium complex, $H_2[ReOCl_5]$, and 5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene (Fig. 1) were prepared by literature methods [11–13]. NaSCN and PPh_3 were BDH products. Ethanol, DMF, 1,4-dioxane, acetone, chloroform, ether, DMSO and HCl were reagent grade chemicals.

Preparation of the Rhenium Complexes

1. A Complex Prepared in 2 N HCl Solution, Molar Ratio M : N_4L, 1 : 1

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The starting Re(V) complex, $H_2[ReOCl_5]$, undergoes hydrolysis in HCl solutions below 6 N, so the following preparation was accomplished by using this concentrated medium and subsequent dilution to 2 N by adding the ligand dissolved in the appropriate amount of water. The rate of formation of the new complex, in this case, is faster than hydrolysis of the Re(V) complex.

$[Re_2O_3(N_4L)_2]Cl_4 \cdot 2H_2O$ (**I**) Eighty mL of 0.0502 M $H_2[ReOCl_5]$ solution, i.e., containing 1.526 g (4.0 mmol) of the starting Re(V) compound in 6 N HCI, was added gradually to 1.008 g (4.0 mmol) of the ligand (N_4L) in 160 mL distilled water. The mixture was stirred for 8 h and then kept at room temperature for two days. The resulting precipitate was filtered, washed with 2 N HCI, chloroform and finally with ether. The complex was soluble in DMF, DMSO and partially soluble in ethanol but insoluble in 1,4-dioxane.

2. Complexes Prepared in 6 N HCl Solutions

Molar Ratio M : N_4L, 1 : 1 $[ReO(N_4L)(OH_2)]Cl_3$ (**II**) Eighty ml of 0.0502 M $H_2[ReOCl_5]$ solution, i.e., containing 1.526 g (4.0 mmol) of the Re(V) compound in 6 N HCI, was added gradually to 1.008 g (4.0 mmol) of the ligand (N_4L) and the

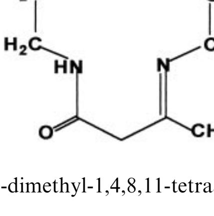

FIGURE 1 5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene, N_4L.

mixture was stirred at room temperature for 9 h, then stored for two days at the same temperature. The resulting precipitate was filtered, washed with 6N HCI, chloroform and finally with ether.

Molar Ratio M : N_4L : PPh_3 1 : 1 : 1 [ReO(N_4L)(PPh_3)]$Cl_3\cdot H_2O$ (**III**) Eighty mL of 0.0502 M $H_2[ReOCl_5]$ solution, i.e., containing 1.526 g (4.0 mmol) of the Re(V) compound in 6 N HCl, was added gradually to a mixture of 1.008 g (4.0 mmol) of the ligand (N_4L) and 1.049 g (4.0 mmol) of PPh_3. The mixture was stirred for 6 h, then kept at room temperature for two days. The resulting precipitate was filtered, washed with 6 N HCI, chloroform then ether.

Molar Ratio M : N_4L : SCN^-, 1 : 1 : 1 [ReO(N_4L)(SCN)]$Cl_2\cdot H_2O$ (**IV**) Eighty mL of 0.0502 M $H_2[ReOCl_5]$ solution in 6 N HCl, was added gradually to a mixture of 1.008 g (4.0 mmol) of ligand (N_4L) and 0.324 g (4.0 mmol) of NaSCN. The mixture was stirred for 8 h and then kept at room temperature for two days. The resulting precipitate was filtered, washed with 6 N HCl, chloroform then ether.

Complexes **II**, **III** and **IV** were soluble in DMF, DMSO and insoluble in 1,4-dioxane. Complex **IV** was soluble in ethanol while complexes **II** and **III** were only partially soluble.

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Physical Measurements and Analyses

Rhenium and chloride ions were determined gravimetrically as nitron-perrhenate and silver chloride, respectively [14]. 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 spectrophotometer using KBr discs with polystyrene calibrant. Far-IR spectra were measured with a Nicolet 20F-FTIR spectrophotometer using polyethylene discs. Magnetic moments were measured by the Gouy method at room temperature using a Johnson Matthey Alfa product, Model No. MKI, magnetic susceptibility balance with $Hg[Co(CNS)_4]$ as calibrant. Diamagnetic corrections were calculated from Pascal's constants [15]. ^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-DSC measurements were carried out on SHIMADZU thermogravimetric analyzer using the TA-50 WSI program. Conductivities were measured on solutions of the complexes in DMF (10^{-3} M) using a Wissenschaftlich-Technische Werkstatten, D8120 Weilheim, Germany, Model LBR 40 A, conductivity meter. Mass spectra were recorded on a Hewlett-Packard mass spectrometer, model MS 5988. Microanalyses of carbon, hydrogen, nitrogen and sulfur were carried out at the Microanalytical Center, Cairo University, Giza, Egypt.

RESULTS AND DISCUSSION

The reactions of $H_2[ReOCl_5]$ with 5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-l,8-diene (N_4L) as a ligand at different concentrations of hydrochloric

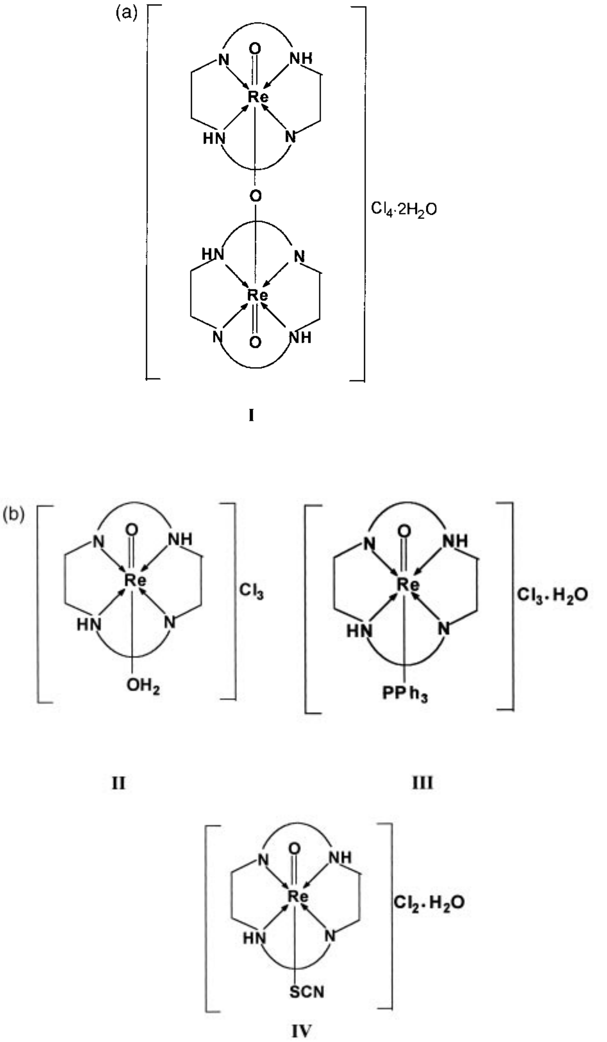

FIGURE 2 Structures of mono- and dinuclear oxorhenium(V) complexes. **I** bis-5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene μ-oxo-dioxodirhenium(V) chloride dihydrate complex. **II** aquo(5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene)oxorhenium(V) chloride complex. **III** triphenylphosphine(5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene) oxorhenium(V) chloride hydrate. **IV** thiocyanato(5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene) oxorhenium(V) chloride hydrate.

acid solutions and at room temperature yielded different products. A mononuclear oxorhenium(V) complex was obtained in a 6 N HCl solution, Fig. 2b (structure **II**). A dinuclear oxorhenium(V) complex was obtained in 2 N HCl solution, Fig. 2a (structure **I**). The reaction of a 1 : 1 mixture of either PPh_3 or NaSCN and N_4L, with $H_2[ReOCl_5$ in 6 N HCl yielded mononuclear oxorhenium(V) complexes, Fig. 2a (structures **III** and **IV**).

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

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TABLE I Elemental analysis of the macrocyclic ligand and its rhenium(V) complexes

Compound	*Color*	*Yield (%)*	*Element analyses (Found/Calcd.)*					
			%C	*%H*	*%N*	*%S*	*%Re*	*%Cl*
N_4L $C_{12}H_{20}O_2N_4$ M.wt = 252.23	White	68	57.30 (57.12)	7.80 (7.98)	21.90 (22.20)	– –	– –	– –
I $[Re_2O_3(N_4L)]Cl_4 \cdot 2H_2O$ $C_{24}H_{44}N_8O_9Re_2Cl_4$ M.wt. = 1102.89	Brownish-black	73	26.00 (26.14)	4.10 (4.02)	15.90 (10.16)	– –	33.53 (33.77)	12.70 (12.86)
II $[ReO(N_4L)(OH_2)]Cl_3$ $C_{12}H_{22}N_4O_4ReCl_3$ M.wt. = 578.90	Pale-brown	65	24.70 (24.90)	3.90 (3.83)	9.50 (9.68)	– –	31.95 (32.16)	18.20 (18.37)
III $[ReO(N_4L)PPh_3]$ $Cl_3 \cdot H_2O$ $C_{30}H_{37}N_4O_4PReCl_3$ M.wt. = 841.20	Canary-yellow	71	43.00 (42.83)	4.40 (4.43)	6.50 (6.66)	– –	22.10 (22.14)	12.55 (12.64)
IV $[ReO(N_4L)(SCN)]Cl_2 \cdot H_2O$ $C_{13}H_{22}N_5SO_4ReCl_2$ M.wt. = 601.52	Yellowish green	62	26.10 (25.96)	3.80 (3.69)	11.50 (11.64)	5.40 (5.33)	31.10 (30.96)	11.84 (11.79)

TABLE II Characterisitc IR bands (cm^{-1})[a] of the macrocyclic ligand and its rhenium(V) complexes

Compound	*νNH*	*νSCN*	*νC=O*	*νC=N*	*νRe=O*	*νRe–N*	*Additional bands*
$N_4L(C_{12}H_{20}O_2N_4)$	3278 br	–	1644 s	1600 s, 1544 m	–	–	–
I	3240 br	–	1650 s	1583 s, 1520 m	911 s	465 m, 432 w	3385 br (lattice water), 714 m, ν_{asymm}(Re–O–Re)
II	3236 br	–	1648 s	1578 s, 1517 m	974 s	467 m, 440 w	3437 br (coordinated water), 627 m ν(Re–O)
III	3245 br	–	1647 s	1573 s, 1522 m	978 s	459 m, 428 w	3370 br (lattice water), 3080 m ν(C–H) aromatic, 310 m ν(Re–P)
IV	3243 br	2057 s	1645 s	1584 s, 1524 m	975 s	462 m, 430 w	3362 br (lattice water), 290 w ν(Re–S)

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

TABLE III Physio-chemical measurements of the start Re(V) complex macrocyclic ligand and its rhenium(V) complexes

Compound	*Molar conductance*[a] (Ohm^{-1}) cm^2 mol^{-1}	*μ eff*[b] (B.M.)	λ^{a}_{max}(nm)
$N_4L(C_{12}H_{20}O_2N_4)$	–	–	219, 279, 292, 342
$H_2[ReOCl_5]$[c]	–	–	420, 480, 780
I	183	0.07	287, 345, 383, 448
II	141	0.12	255, 343, 356, 446
III	137	0.14	257, 340, 254, 410
IV	91	0.09	275, 341, 355, 408

[a] DMF solutions, 1×10^{-3} M, at 30°C.
[b] Measurements were performed at 26°C.
[c] A solution of the start complex in 6 N HCl was used.

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TABLE IV ^{1}H NNIR of the macrocyclic ligand and its rhenium(V) complexes

Compound	*δ NH*[a]	*δ CH_2 (diaminoethane)*	*δ CH_2 (alkylacetate)*
$N_4L(C_{12}H_{20}O_2N_4)$	7.50–7.90(2H)	3.15(8H)	2.15(4H)
I	8.30(4H)	3.18(16H)	2.10(8H)
II	8.53(2H)	3.14(8H)	2.12(4H)
III	8.62(2H)	3.16(8H)	2.14(4H)
IV	8.57(2H)	3.20(8H)	2.12(4H)

[a] Chemical shifts with reference to TMS.

TABLE V Thermal analysis of rhenium(V) complexes

Compound	*Temperature range °C*	*%Loss in weight Actual (Calc.)*	*DSC Peak °C*		*Δ H*, J/g	*Composition of the residue*	*Probable composition of expelled groups*
			Endo.	*Exo.*			
I	50–110	3.15(3.26)	106	–	5.70	$[Re_2O_3(N_4L)_2]Cl_4$	Two molecules of lattice water
II	110–370	16.60(16.49)	–	357	– 4.47	$[Re_2O_3(N_4L^{\backslash})_2]$	Four molecules of HCl
III	150–312	3.20(3.11)	–	296	– 14.37	$[ReO(N_4L)Cl]Cl_2$	One molecule of coordinated water
IV	60–360	48.15(47.43)	–	354	– 36.50	$[Re_2O_3(N_4L^{\backslash})_2]$	Two molecules of lattice water, two molecules of PPh_3 and six molecules of HCl out of two complex molecules
V	45–96	3.10(2.99)	86	–	2.51	$[ReO(N_4L)(SCN)]Cl_2$	One molecule of lattice water
	96–430	15.00(15.12)	–	425	– 53.55	$[ReO(N_4L^{\backslash})(SCN)]$	Two molecules of HCl

$N_4L^{\backslash}$ = The dianionic ligand, due to dissociation of two hydrogen atoms of two NH groups.

IR Spectra

The IR spectra of the free ligand (N_4L) and its complexes are listed in Table II. The IR spectrum of the free ligand (N_4L) shows characteristic bands for νNH (3278 cm^{-1}), νC=O (1644 cm^{-1}) and νC=N (1600, 1544 cm^{-1}). In all complexes, νNH was shifted (30–40 cm^{-1}) to lower frequencies, due to coordination of the NH groups. Also, νC=N were shifted (16–27 cm^{-1}) to lower frequencies, due to participation of azomethine groups in coordination. On the other hand, the stretching vibration of νC = O was unaffected in all complexes, which indicates that the carbonyl groups are not involved in coordinating the metal cation.

The participation of the nitrogen atoms of the ring, from the NH and C=N groups, was also confirmed by appearance of new bands in the range 428–467 cm^{-1} attributed to νRe–N [16]. The νRe=O band occurs at 974–978 cm^{-1}, for the mononuclear complexes and at 911 cm^{-1} for the dinuclear complex, consistent with values previously cited in the literature for similar mono- and dinuclear complexes [17–22]. The IR spectrum of the dinuclear oxorhenium(V) complex **I**, structure **I** in Fig. 2a, shows a new band at 714 cm^{-1}, indicating the presence of a bridging oxygen atom linking the two rhenium(V) cations (Re–O–Re) [20,23].

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The stretching vibration of the coordinated water molecule appears at $3437\,cm^{-1}$ for complex **II**. Also, a new band appears in the region $672\,cm^{-1}$ due to the Re–O linkage between the metal cation and the oxygen atom of the coordinated water molecule [17,20]. Complexes **I**, **III** and **IV** showed broad bands at 3385, 3370 and $3362\,cm^{-1}$, respectively, due to H-bonded lattice water molecules. The mononuclear complex **III**, Structure **III** in Fig. 2b, shows the νC–H aromatic stretch in the region $3080\,cm^{-1}$ and a new band at $310\,cm^{-1}$ due to νRe–P which confirms the coordination of PPh_3 group in the inner sphere of the complex. The IR spectrum of the mononuclear complex **IV**, structure **IV** in Fig. 2b, showed a new strong band at $2057\,cm^{-1}$, which indicates the coordination of the SCN group to the rhenium cation via the sulfur atom [18,20,24]. The Re–S stretching frequency appears at low frequency, $290\,cm^{-1}$.

UV Visible Spectra

The UV spectrum of the free ligand shows four absorption bands at 219, 279, 292 and 342 nm, Table III. The visible spectrum of the starting rhenium complex (d^2) shows a main band at 780 nm. The prepared rhenium complexes show four bands at 255–287, 340–345, 354–383 and 408–448 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 $d\pi(Re)\rightarrow\pi^*(L)$ and in the UV region is assigned to intraligand $\pi\rightarrow\pi^*$ [25].

Magnetic Moments

The oxo complexes of rhenium(V) are all diamagnetic [26]. The magnetic moments of rhenium(V) complexes, Table III, confirm their diamagnetic character.

Conductivity Measurements

Conductivity measurements, Table III, indicate that complexes **I**, **II**, **III** and **IV** are 1 : 4, 1 : 3, 1 : 3 and 1 : 2 electrolytes, respectively. The relatively low values of the measured conductivities may be due to the bulky cations which contain the Re=O(V) ion.

Nuclear Magnetic Resonance Spectral Studies

The assignment of the main signals in the ^1H NMR spectra of the macrocyclic ligand (N_4L) and its rhenium(V) complexes are listed in Table IV. The free ligand (N_4L) showed broad signals at δ 7.50–7.90 ppm (2H) due to the amide protons [27], δ 3.15 ppm (8H) of CH_2 (diaminoethane) and δ 2.15 ppm (4H) of CH_2 (alkylacetate).

In all complexes (**I**–**IV**), the signal corresponding to the amide protons is shifted downfield (8.30–8.62) due to strong deshielding by the metal cation. The signals corresponding to CH_2(diaminoethane) and CH_2(alkylacetate) are shifted slightly downfield or upfield from the free ligand (N_4L).

Thus the ^1H NMR and IR spectra suggest that the mode of coordination of ligand (N_4L) is through the nitrogen atoms of the ring when it acts as a neutral tetradentate ligand, consistent with previous work on this ligand with other transition metal cations [13,28].

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Mass Spectra

Mass spectral data are consistent with the formulation $[ReO(N_4L)(OH_2)]Cl_3$ **(II)**, $[ReO(N_4L)PPh_3)]Cl_3$ **(III)** and $[ReO(N_4L)(SCN)]Cl_2$ **(IV)**, which give the parent ions at *m/e* 579 a.m.u. (calculated value 578.90 a.m.u.), 824.05 a.m.u. (calculated value 823.20 a.m.u. after subtracting one molecule of lattice water) and 584.36 a.m.u. (calculated value 583.52 a.m.u. after subtracting one molecule of lattice water), respectively.

The mass spectrum of complex **II**, shows the presence of a mass fragment corresponding to $ReO(C_{12}H_{20}O_2N_4)Cl_3^+$, *m/e* 559.50 (28.89%), which loses Cl atom to give the fragment $ReO(C_{12}H_{20}O_2N_4)Cl_2^+$, *m/e* 524.05 (31.11%), followed by the loss of 2CO molecules to give the fragment $ReO(C_{10}H_2ON_4)Cl_2^+$, *m/e* 467.95 (28.89%). Also there is a fragment corresponding to ReO^+ at *m/e* 202.05 (28.89%).

Complex **III** shows the presence of a mass fragment corresponding to $ReO(C_{12}H_{20}O_2N_4)PPh_3)Cl_2^+$, *m/e* 787.08 (35.42%), which loses 2CO molecules to give the fragment $ReO(C_{10}H_{20}N_4)(PPh_3)Cl_2^+$, *m/e* 730.75 (22.92%) then loses 2C1 atoms to give the fragment $ReO(C_{10}H_{20}N_4)(PPh_3)^+$, *m/e* 660.52 (25.0%), followed by the loss of PPh_3 give the fragment $ReO(C_{10}H_{20}N_4)^+$, *m/e* 398.52 (27.08%) and finally the fragment due to ReO^+ is present at *m/e* 202.90 (20.83%).

The mass spectrum of complex **IV** shows the presence of a mass fragment corresponding to $ReO(C_{12}H_{20}O_2N_4)(SCN)Cl^+$, *m/e* 548.14 (16.67%), which loses 2CO molecules to give the fragment $ReO(C_{10}H_{20}N_4)(SCN)Cl^+$, *m/e* 492.15 (21.67%), then loses a Cl atom to give the fragment $ReO(C_{10}H_{20}N_4)(SCN)^+$, *m/e* 456.84 (16.60%), followed by the loss of $2CH_3$ groups then the HSCN molecule to give the fragment $ReO(C_8H_{13}N_4)^+$, *m/e* 367.30 (23.33%). The fragment $ReO(N_4L)(SCN)Cl^+$, loses a HCl molecule followed by a HSCN molecule to give the fragment $ReO(C_{12}H_{18}O_2N_4)^+$, *m/e* 451.75 (16.90%). The fragmentation pattern of the complex **IV** is shown in Scheme I.

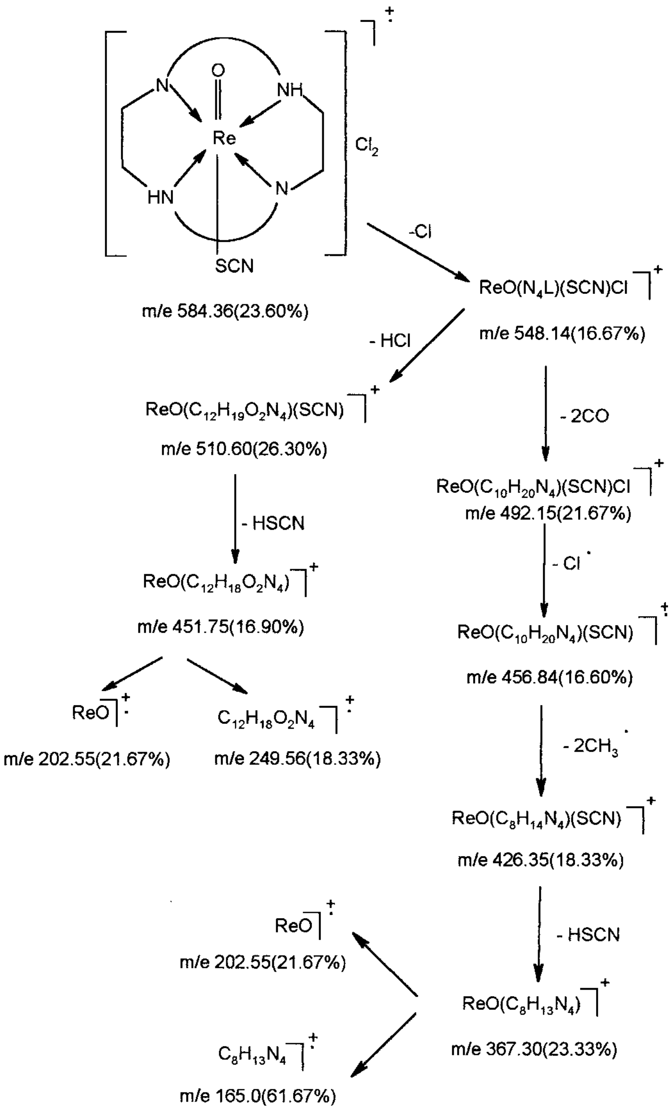
Thermal Analyses

The results of TG-DSC analyses of the complexes are shown in Table V. The loss of the water of crystallization in complexes **I** and **IV** occurs in the temperature range 45–110°C. Elimination of lattice water was accompanied by an endothermic peak with ΔH, 5.70 and 2.51 J/g, respectively. Complex **III** loses two molecules of PPh_3, six molecules of HCl besides two molecules of lattice water out of two complex molecules, in one step, to give the isolable complex $[Re_2O_3(N_4L^{\backslash})_2]$ at 354°C.

The coordinated water molecules in complex **II** were eliminated in the temperature range 150–312°C and there is an exothermic peak at 296°C with ΔH, −14.37 J/g. This exothermic process may be due to chloride transfer from the outer to inner sphere of the complex. Complexes **I** and **IV** also lose HCl molecules at 370 and 430°C, respectively. HCl molecules were eliminated from chloride ions and protons from the NH groups of the ligand N_4L, thus the ligand changes to $(N_4L^{\backslash})$.

Pyrolytic Preparations and Characterization of some Rhenium(V) Complexes

New solid oxorhenium(V) complexes were prepared pyrolytically from the mother complexes **I–IV**. Structures of the obtained products are discussed on the basis of their IR spectra, conductivity measurements and elemental analyses for rhenium and chloride.



SCHEME 1 Fragmentation pattern of complex **IV**

$[Re_2O_3(N_4L)_2]$ was prepared by heating either complex **I** to 357°C or complex **III** to 354°C until constant weight. The color of the complex was black and differed from the colors of both starting complexes. Its IR spectrum showed bands assigned to νRe=O at 909 cm^{-1} and νRe–O–Re at 711 cm^{-1}, which indicates that the complex is dinuclear [12,20,23]. Also, it showed bands at 1589 and 1524 cm^{-1}, due to vC=N, and at 469 and 437 cm^{-1}, due to νRe–N. The νNH in the starting complexes disappeared in the heated product, due to dissociation of the protons of the NH groups and thus the ligand behaves as a dianionic tetradentate ligand. The elemental analysis and conductivity of its DMF solution indicated that the heated product is a non-electrolyte and thus the chloride ions were lost.

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From the previous results and the elemental analysis of rhenium, the product obtained on heating can be represented as $[Re_2O_3(N_4L^\backslash)_2]$ and its proposed structure is shown in Fig. 3.

$[ReO(N_4L)Cl]Cl_2$ was prepared by heating complex **II** at 296°C to a constant weight; the color changed from pale-brown to greenish-gray. Its IR spectrum showed a band assigned to νRe=O at 979 cm^{-1}, which indicates that the complex is mononuclear [23]. The band due νRe–O of the coordinated water molecule at 672 cm^{-1} disappeared, while a new band due to νRe–Cl was observed at 362 cm^{-1}. The νNH was observed at 3238 cm^{-1}, which indicates that the ligand (N_4L) is still neutral tetradentate. The coordination of the chloride ion was also confirmed by conductivity measurements in DMF solution which showed a lowering in the molar conductance (93 $Ohm^{-1} cm^2 mol^{-1}$) in comparison to complex **II**.

From the previous results and the elemental analyses of rhenium and chlorine, this product can be represented as $[ReO(N_4L)Cl]Cl_2$ and its proposed structure is as shown in Fig. 4.

$[ReO(N_4L^\backslash)(SCN)]$ was also prepared by heating complex **IV** at 425°C to constant weight; the color changed from yellowish-green to gray. The IR spectrum of the heated product showed only one band at 977 cm^{-1} due to νRe=O, which indicates that the complex is mononuclear [23]. The νNH disappeared in the heated product and the elemental analysis of chlorine showed the absence of chloride ions which indicates the dissociation of the protons of the NH groups in the form of HCl and

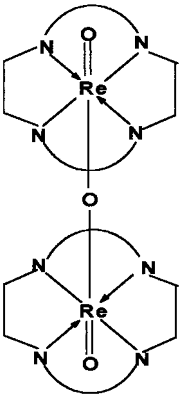

FIGURE 3 Structure of $[Re_2O_3(N_4L^\backslash)_2]$,bis-5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene-μ-oxo-dioxodirhenium(V) complex, obtained by heating either complex **I** to 357°C or complex **III** to 354°C.

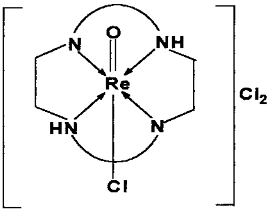

FIGURE 4 Structure of $[ReO(N_4L)Cl]Cl_2$ chloro-bis(5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene) oxorhenium(V) chloride complex obtained by heating complex **II** to 296°C.

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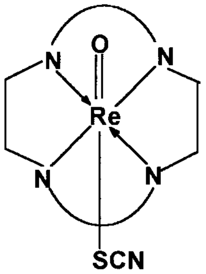

FIGURE 5 Structure of [ReO(N_4L)(SCN)], thiocyanatobis(5,12-dioxa-7,14-dimethyl-1,4,8,11-tetraaza-cyclotetradeca-1,8-diene) oxorhenium(V) complex, obtained by heating complex **IV** to 425°C.

the ligand is dianionic tetradentate. The band corresponding to νSCN appears at $2059\,cm^{-1}$, indicating that the thiocyanate anion is still coordinated via sulfur. The conductance of a DMF solution of this product proved that it is a non-electrolyte. From the previous results and elemental analysis of rhenium this product can be represented as [ReO(N_4L)(SCN)] and its structure is as proposed in Fig. 5.

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CONCLUSION

The reactions of the tetraaza macrocyclic ligand N_4L with the oxorhenium(V) complex, $H_2[ReOCl_5]$ in 6 N HCl solution yielded dinuclear complex **I** when the [HCl] was decreased to 2 N and a mononuclear complex **II** at its ordinary concentration, 6 N. It also yielded mixed ligand oxorhenium complexes **III** and **IV** when the tetraaza macrocyclic ligand was mixed with either KSCN or PPh_3 ligands in 6 N HCl solution. The structures of the obtained complexes indicated that the tetraaza macrocycle is a neutral tetradentate ligand through its four nitrogen atoms of the macrocyclic ring, while both PPh_3 and SCN are monodentate.

Thermal studies on the above complexes **I–IV** revealed the possibility of obtaining other solid complexes by heating these complexes to certain temperatures. However, these new thermal complexes cannot be prepared directly in solution from the starting ligands and oxorhenium(V) complex. Three of these thermal products were obtained; in one the tetraaza macrocyclic ligand retained its NH groups and yielded a mononuclear complex. In the other two thermal products, the tetraaza macrocyclic ligand lost the hydrogen atoms of its NH group. One of the latter complexes was mononuclear and the other was dinuclear and in both the tetraaza macrocycle was a dianionic tetradentate ligand. It thus seems that the tetraaza macrocyclic ligand loses it hydrogen atoms of the NH groups at relatively high temperatures, i.e., above ~320°C.

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