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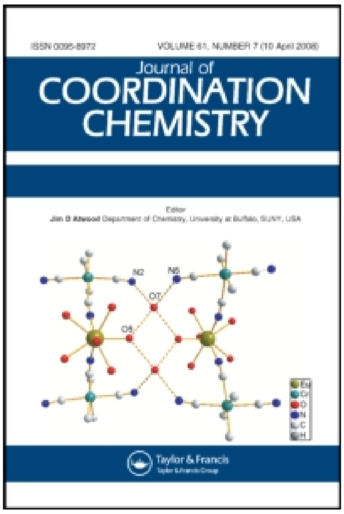

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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Online publication date: 15 September 2010

To cite this Article Mashaly, Mahmoud M.(2003) 'Oxorhenium(V) Complexes Derived from 8,17-Dimethyl-6,15-Dioxo-5,7,14,16-Tetrahydrodibenzo[a,h][14] Annulene-2,11-Dicarboxylic Acid and their Pyrolytical Products', Journal of Coordination Chemistry, 56: 10, 833 — 850

To link to this Article: DOI: 10.1080/0095897031000114011

URL: http://dx.doi.org/10.1080/0095897031000114011

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J. Coord. Chem., Vol. 56, No. 10, 10 July 2003, pp. 833–850

OXORHENIUM(V) COMPLEXES DERIVED FROM 8,17-DIMETHYL-6,15-DIOXO-5,7,14,16-TETRAHYDRODIBENZO[a,h][14] ANNULENE-2,11-DICARBOXYLIC ACID AND THEIR PYROLYTICAL PRODUCTS

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(Received 7 August 2002; Revised 14 November 2002; In final form 8 March 2003)

A new series of oxorhenium(V) complexes were prepared by reaction of 8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid(H_4L), alone or with addition of PPh_3 or NaSCN, with $H_2[ReOCl_5]$. Mononuclear complexes, $[ReO(H_4L)Cl]Cl_2$, $[ReO(H_4L)(PPh_3)]Cl_3$, and $[ReO(H_4L)(SCN)]Cl_2$ were obtained in 6 N HCl, while the binuclear complex, $[Re_2O_3(H_4L)_2]Cl_4$ was obtained in 2 N HCl. Thermal studies on these complexes showed the possibility of obtaining new complexes pyrolytically, where the complexes decompose through several isolable as well as nonisolable, intermediates during heating. $[Re_2O_3(H_2L)_2]$, $[ReO(H_2L)Cl]$, $[ReO(H_2L)(PPh_3)]Cl$, and $[ReO(H_2L)(SCN)]$, were synthesized pyrolytically in the solid state from the respective precursor rhenium complexes. All of the prepared complexes and their thermal products have octahedral configurations. The ligand (H_4L) behaves either as a neutral tetradentate or dianionic tetradentate ligand towards the oxorhenium ions in these complexes. The carboxylate groups are not coordinated to oxorhenium ions, which was checked by the acidity test and/or addition of metal ions such as Cu(II) and Ni(II), where a variety of new complexes coordinated via carboxylate groups were obtained. The screening of antibacterial and antifungal activities on the free ligand and all complexes, showed higher antifungal activities against *Alternaria alternata* than against *Aspergillus fumigatus*. The structures of all complexes and the corresponding thermal products 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 spectrometry.

Keywords: Rhenium; Oxo; Macrocycle; Antifungal; Antibacterial

INTRODUCTION

Polyaza macrocyclic ligands, in their protonated forms, have been shown to bind certain neutral molecules and anions in solution [1–4] and in some instances to catalyze biologically significant reactions of the bound substrates [5–7].

8,17-Dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid, abbreviated as H_4L, has structures resembling porphyrins(H_2TTP) and

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/0095897031000114011

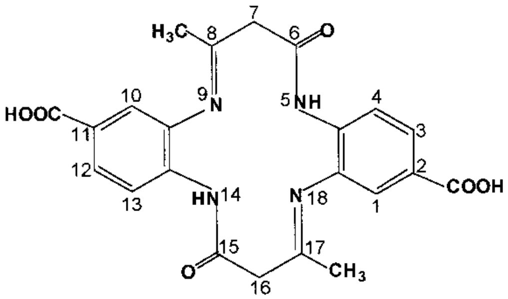


FIGURE 1 8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid, H_4L.

phthalocyanines(H_2Pc). The aza crowns 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 engaged in coordination and not the oxygen [8–10].

Rhenium complexes are excellent structural models for Tc complexes because ^{99}Tc and Re complexes have essentially identical coordination parameters and Re is a nonradiative element [11–13]. The coordination chemistry of rhenium and technetium are of considerable interest due to the widespread use of $^{186/188}$Re and ^{99m}Tc isotopes as therapeutic agents and diagnostic imaging agents, respectively, in nuclear medicine [14–16].

The antibacterial and antifungal activities of the transition metal complexes derived from semicarbazones and thiosemicarbazones have been studied widely [17–21].

We have previously reported [22–27] on the synthesis and characterization of complexes of oxorhenium(V) with Lewis bases (N- and/or S-donor). In continuation of this work, 8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid (Fig. 1) was used as a nitrogen donor ligand. The reactions of this ligand alone and/or mixed with PPh_3 and/or NaSCN with the starting rhenium(V) complex gave variable forms of complexes depending on the concentration of hydrochloric acid containing the starting metal complex.

The thermal studies explored the possibility of synthesizing some new oxorhenium(V) complexes which cannot be synthesized from solution pyrolytically in the solid state.

EXPERIMENTAL

$H_2[ReOCl_5]$ was prepared by a literature method [28,29]. NaSCN, PPh_3, ethylacetoacetate, and 3,4-diaminobenzoic acid were BDH products. Ethanol, methanol, DMF, 1,4-dioxane, acetone, chloroform, ether, DMSO, and HCl were reagent grade chemicals.

Preparation of H_4L {8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic Acid}

A solution of ethylacetoacetate (1.30 g, 10 mmol) in methanol (40 mL) was added to a magnetically stirred solution of 3,4-diaminobenzoic acid (1.52 g, 10 mmol) in methanol (40 mL). The resulting mixture was stirred for 5 h, then kept for 10 h at room temperature and a pale brown crystalline compound precipitated. The product was washed with methanol and dried *in vacuo*. The isolated ligand H_4L exists in one isomer, checked by TLC.

Preparation of the Rhenium Complexes

Complex Prepared in 2 N HCl Solution, Molar Ratio M : H_4L, 1 : 1

The starting Re(V) complex, $H_2[ReOCl_5]$, undergoes hydrolysis in HCl solutions below 6 N. The following preparation uses 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.

$[Re_2O_3(H_4L)_2]Cl_4$ (I) 60 mL of 0.05 M $H_2[ReOCl_5]$ solution, i.e. containing 1.14 g (3.0 mmol) of the starting Re(V) compound in 6 N HCl, was added gradually to 1.31 g (3.0 mmol) of the ligand (H_4L) in 120 mL distilled water. The mixture was stirred for 10 h, then kept at room temperature for two days. The resulting precipitate was filtered, washed with 2 N HCl, chloroform and finally with ether. The product isolated was 1.79 g (66%) of a brown solid. The complex was soluble in DMF, DMSO, and ethanol but insoluble in 1,4-dioxane.

Complexes Prepared in 6 N HCl Solutions

Molar Ratio M : H_4L, 1 : 1 $[ReO(H_4L)Cl]Cl_2$ (II) 60 mL of 0.05 M $H_2[ReOCl_5]$ solution, i.e. containing 1.14 g (3.0 mmol) of the starting Re(V) compound in 6 N HCl, was added gradually to 1.31 g (3.0 mmol) of the ligand (H_4L) and the mixture was stirred at room temperature for 12 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. The product isolated was 1.38 g (62%) of a brownish-violet solid.

Molar Ratio M : H_4L : PPh_3, 1 : 1 : 1 $[ReO(H_4L)(PPh_3)]Cl_3$ (III) 60 mL of 0.05 M $H_2[ReOCl_5]$ solution, i.e. containing 1.14 g (3.0 mmol) of the Re(V) compound in 6 N HCl, was added gradually to a mixture of 1.31 g (3.0 mmol) of the ligand (H_4L) and 0.79 g (3.0 mmol) of PPh_3. 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 then ether. The product obtained was 2.08 g (69%) of a greenish-brown solid.

Molar Ratio M : H_4L : SCN^-, 1 : 1 : 1 $[ReO(H_4L)(SCN)]Cl_2$ (IV) 60 mL of 0.05 M $H_2[ReOCl_5]$ solution, i.e. containing 1.14 g (3.0 mmol) of the start Re(V) compound in 6 N HCl, was added gradually to a mixture of 1.31 g (3.0 mmol) of ligand (H_4L) and 0.24 g (3.0 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. The product obtained was 1.49 g (65%) of a pale-pink solid.

Complexes **II**, **III**, and **IV** were soluble in DMF, DMSO and insoluble in 1,4-dioxane. Complex **II** and **IV** were also soluble in ethanol while Complex **III** was partially soluble. Table I indicates the colors, % yield, and elemental analysis data of the ligand H_4L and its rhenium(V) complexes.

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

Compound	*F.W*	*Color*	*Yield %*	*Elemental analysis found (calc.)*						
				%C	*%H*	*%N*	*%S*	*%Re*	*%Cl*	*%P*
H_4L	436.42	Pale brown	72	60.20	4.70	12.70	–	–	–	–
$C_{22}H_{20}N_4O_6$				(60.55)	(4.62)	(12.84)	–	–	–	–
I $[Re_2O_3(H_4L)_2]Cl_4$	1435.07	Brown	66	36.90	2.70	7.60	–	25.80	10.00	–
$C_{44}H_{40}N_8O_{15}Re_2Cl_4$				(36.82)	(2.81)	(7.81)	–	(25.95)	(9.88)	–
II $[ReO(H_4L)Cl]Cl_2$	744.99	Brownish-violet	62	35.50	2.80	7.40	–	24.70	14.40	–
$C_{22}H_{20}N_4O_7ReCl_3$				(35.47)	(2.70)	(7.52)	–	(24.99)	(14.27)	–
III $[ReO(H_4L)(PPh_3)]Cl_3$	1007.28	Greenish-brown	69	41.40	3.60	5.40	–	18.50	10.70	2.90
$C_{40}H_{35}N_4O_7PReCl_3$				(41.69)	(3.50)	(5.56)	–	(18.48)	(10.56)	(3.07)
IV $[ReO(H_4L)(SCN)]Cl_2$	767.62	Pale pink	65	36.20	2.60	9.00	4.00	24.30	9.40	–
$C_{23}H_{20}N_5O_7SReCl_2$				(35.99)	(2.62)	(9.12)	(4.18)	(24.26)	(9.24)	–
V $[Re_2O_3(H_2L)_2]$	1289.23	Black	88	40.70	2.70	8.50	–	28.80	–	–
$C_{44}H_{36}N_8O_{15}Re_2$				(40.99)	(2.81)	(8.69)	–	(28.89)	–	–
VI $[ReO(H_2L)Cl]$	672.07	Deep green	80	39.50	2.60	8.00	–	27.60	5.40	–
$C_{22}H_{18}N_4O_7ReCl$				(39.32)	(2.70)	(8.34)	–	(27.71)	(5.27)	–
VII $[ReO(H_2L)(PPh_3)]Cl$	984.36	Greenish-gray	92	51.30	3.50	5.80	–	19.90	3.90	3.00
$C_{40}H_{33}N_4O_7PReCl$				(51.42)	(3.56)	(6.00)	–	(19.93)	(3.79)	(3.31)
VIII $[ReO(H_2L)(SCN)]$	694.70	Deep brown	90	39.80	2.50	10.00	4.50	26.70	–	–
$C_{23}H_{18}N_5O_7SRe$				(39.76)	(2.61)	(10.08)	(4.61)	(26.80)	–	–

Physcial 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 spectrophotometer using KBr discs with polystyrene as calibrant. Fair-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, Model No. MKI, magnetic susceptibility balance, $Hg[Co(CNS)_4]$ was used as a calibrant. Diamagnetic corrections were calculated from Pascal's constants [30]. ^{1}H-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 in a dry atmosphere and with a heating rate of 10 deg/min using TA-50 WSI program. Conductivities were measured in solutions of the complexes in DMF (10^{-3} M) using a Wissenschaftlich-Technische Werkstatten, D8120 Weilheim, Germany, Model LBR 40A, conductivity meter. Mass spectra were recorded on a Hewlett-Packard mass spectrometer, model MS 5988. Microanalyses of carbon, hydrogen, nitrogen, phosphorus, and sulfur were carried out at the Microanalytical Center, Cairo University, Giza, Egypt. Rhenium and chloride ions were determined gravimetrically as nitro-perrhenate and silver chloride, respectively [31].

RESULTS AND DISCUSSION

The reactions of $H_2[ReOCl_5]$ with the ligand 8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid (H_4L) at different concentrations of hydrochloric acid solution and at room temperature yielded different products. A mononuclear oxorhenium(V) complex was obtained in a 6 N HCl solution, Fig. 2(b) (Structure **II**). A dinuclear oxorhenium(V) complex was obtained in 2 N HCl solution, Fig. 2(a) (Structure **I**). The reaction of a 1 : 1 mixture of either PPh_3 or NaSCN and H_4L, with $H_2[ReOCl_5]$ in 6 N HCl yielded mononuclear oxorhenium(V) complexes, Fig. 2(b) (Structures **III** and **IV**).

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

The following equations illustrate the formation of the complexes obtained

In 2 N HCl Solutions

$$2H_2[ReOCl_5] + 2H_4L + H_2O \rightarrow \underset{\textbf{I}}{[Re_2O_3(H_4L)_2]Cl_4} + 6HCl$$

In 6 N HCl Solutions

$$H_2[ReOCl_5] + H_4L \rightarrow \underset{\textbf{II}}{[ReO(H_4L)Cl]Cl_2} + 2HCl$$

$$H_2[ReOCl_5] + H_4L + PPh_3 \rightarrow \underset{\textbf{III}}{[ReO(H_4L)(PPh_3)]Cl_3} + 2HCl$$

$$H_2[ReOCl_5] + H_4L + NaSCN \rightarrow \underset{\textbf{IV}}{[ReO(H_4L)(SCN)]Cl_2} + NaCl + 2HCl$$

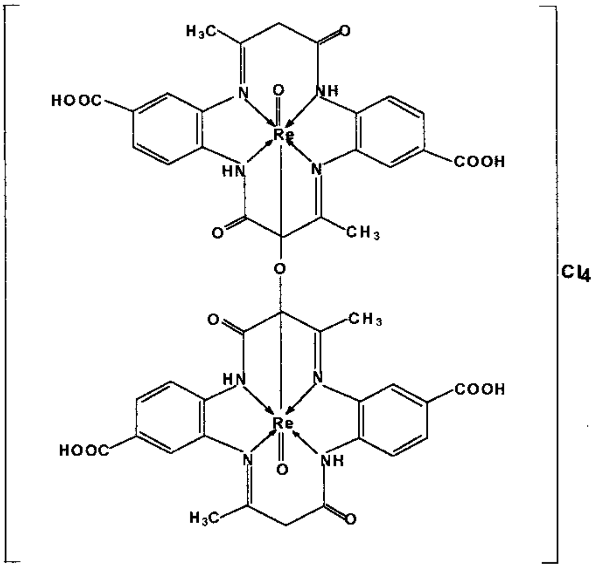
IR SPECTRA

The IR spectra of the free ligand (H_4L) and its complexes are listed in Table II. The IR spectrum of the free ligand (H_4L) shows characteristic bands for νOH (3428 cm^{-1}) and νC=O (1679 cm^{-1}) due to the carboxylic groups. In all complexes the stretching vibrations due to carboxylic groups were unaffected, which indicates that these groups are not involved in coordinating the metal cation. Also the carbonyl groups of alkylacetate (1632 cm^{-1}) were unaffected in all complexes.

The νNH (3327 cm^{-1}) of the free ligand was shifted (122–144 cm^{-1}) to lower frequencies in its complexes, due to coordination of the NH groups. The νC=N observed in the free ligand at 1593 and 1554 cm^{-1} and were shifted (18–50 cm^{-1}) to lower frequencies in its complexes, due to the participation of azomethine groups in coordination.

The participation of the nitrogen atoms of the ring, from the NH and C=N groups, was also confirmed by the appearance of new bands in the range 431–467 cm^{-1} attributed to νRe–N [32]. The νRe=O band occurs at 967–970 cm^{-1}, for the mononuclear complexes and at 912 cm^{-1} for the dinuclear complex, consistent with the values previously cited in the literature for similar mono- and dinuclear complexes [22–27, 33–37]. The IR spectrum of the dinuclear oxorhenium(V) complex **I**, structure **I** in Fig. 2(a), shows a new band at 715 cm^{-1}, indicating the presence of a bridging oxygen atom linking the two rhenium(V) cations (Re–O–Re) [22–25, 38].

(a)



I

FIGURE 2 Proposed structures of mono- and dinuclear oxorhenium(V) complexes. **I** bis-8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid μ-oxo-dioxodirhenium(V) chloride complex. **II** chloro(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid) oxorhenium(V) chloride complex. **III** triphenylphosphine(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid) oxorhenium(V) chloride. **IV** thiocyanato-(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid) oxorhenium (V) chloride.

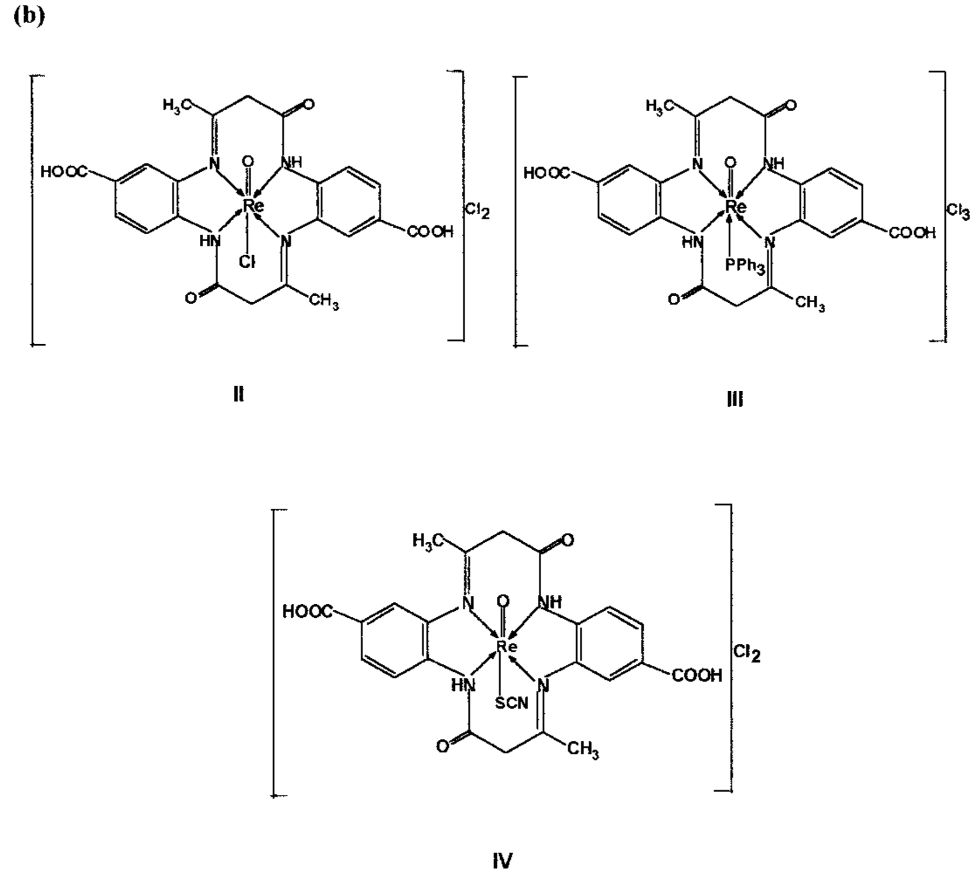


FIGURE 2 Continued.

The IR spectrum of the mononuclear Complex **IV**, Structure **IV** in Fig. 2(b), showed a new strong band at 2055 cm^{-1}, which indicates coordination of the SCN group to the rhenium cation via the sulfur atom [14–18, 31]. The Re–S stretching frequency appears at low frequency, 292 cm^{-1} [22–26, 39]. The mononuclear Complex **III**, Structure **III** in Fig. 2(b), shows a new band at 308 cm^{-1} due to νRe–P [40] which confirms coordination of PPh_3 group in the inner sphere of the complex. The stretching vibration due to νRe–Cl was observed at 359 cm^{-1} [41] for Complex **II**.

UV–Visible Spectra

The UV–Visible spectrum of the free ligand shows three absorption bands at 287, 329, and 364 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 277–288, 325–338, 355–365, and 408–440 nm. The blue-shift of the visible bands in these complexes indicates the replacement of chloride ions by ligand molecules. The bands observed in the visible range are attributed to the charge transfer transition from the oxygen atom to the rhenium atom of the oxorhenium cation [35].

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

Compound	*ν OH*	*ν NH*	*ν SCN*	*ν C=O*	*ν C=N*	*ν Re=O*	*ν Re–N*	*Additional bands*
H_4L ($C_{22}H_{20}O_6N_4$)	3428 br	3327 br	–	1679 s, 1632 s	1593 m, 1554 s	–	–	–
I	3424 br	3205 br	–	1680 s, 1629 s	1575 s, 1509 s	912 s	467 m, 431 w	715 m, ν_{asymm} (Re–O–Re)
II	3425 br	3183 br	–	1679 s, 1630 m	1574 s, 1509 s	969 s	466 m, 432 m	359 m, ν (Re–Cl)
III	3424 br	3192 br	–	1679 s, 1627 m	1575 s, 1509 s	970 s	463 m, 434 m	308 m, ν (Re–P)
IV	3427 br	3188 br	2055 s	1679 s, 1630 m	1575 s, 1508 s	967 s	467 m, 432 m	292 w, ν (Re–S)
V	3426 br	–	–	1678 s, 1628 s	1573 s, 1507 s	914 s	469 m, 433 m	714 m, ν_{asymm} (Re–O–Re)
VI	3427 br	–	–	1679 s, 1629m	1575 s 1506 s	970 s	468 m, 436 m	363 m, ν (Re–Cl)
VII	3426 br	–	–	1677 s, 1630 m	1575 s, 1508 s	972 s	466 m, 435 m	309 m, ν (Re–P)
VIII	3425 br	–	2057 s	1679 s, 1631 m	1572 s, 1504 s	969 s	465 m, 430 m	290 w, ν (Re–S)

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

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

Compound	*Molar conductance*[a] (Ω^{-1} cm^{2}mol^{-1})	μ_{eff^b} (B.M.)	λ_{max^a} (nm)	δ *COOH*[d]	δ *NH*	δ *CH$_2$* *(alkylacetate)*
H_4L ($C_{22}H_{20}O_6N_4$)	–	–	287, 329, 364	14.20 (2H)	7.80–8.06 (2H)	2.09 (4H)
$H_2[ReOCl_5)]$[c]	–	–	420, 480, 780	–	–	–
I	187	0.05	277, 325, 355, 408	14.16 (4H)	8.47 (4H)	2.10 (8H)
II	94	0.07	288, 337, 362, 423	14.22 (2H)	8.45 (2H)	2.08 (4H)
III	139	0.09	277, 337, 365, 415	14.12 (2H)	8.48 (2H)	2.11 (4H)
IV	92	0.12	286, 338, 361, 440	14.17 (2H)	8.46 (2H)	2.12 (4H)
V	6	0.08	267, 337, 363, 422	14.23 (2H)	–	2.08 (8H)
VI	10	0.09	289, 327, 360, 438	14.16 (2H)	–	2.12 (4H)
VII	46	0.07	272, 337, 363, 423	14.20 (2H)	–	2.14 (4H)
VIII	9	0.14	289, 337, 362, 419	14.25 (2H)	–	2.10 (4H)

[a]DMF solutions, 1×10^{-3} M, at 28°C; [b]Measurements were taken at 27°C; [c]A solution of the starting complex in 6N HCl was used; [d]Chemical shifts with reference to TMS.

TABLE IV Thermal analysis or rhenium(V) complexes

Compound	*Temperature range* °C	*% Loss in weight actual (calc.)*	*DSC peak* °C		ΔH, J/g	*Composition of the residue*	*Probable composition of the expelled groups*
			Endo.	*Exo.*			
I	50–353	10.3 (10.17)	353	–	4.33	$[Re_2O_3(H_2L)_2]$	Four molecules of HCl
	353–590	22.1 (22.44)	542	–	17.13	$[Re_2O_3(C_{20}H_{18}O_2N_4)_2]$	Four molecules of CO_2
II	50–307	10.0 (9.80)	305	–	31.80	$[ReO(H_2L)Cl]$	Two molecules of HCl
III	50–233	7.2 (7.25)	227	–	17.70	$[ReO(H_2L)(PPh_3)]Cl$	Two molecules of HCl
	233–310	33.5 (33.28)	–	308	– 12.70	$[ReO(H_2L)Cl]$	One molecule of PPh_3
	310–387	42.3 (42.02)	367	–	4.62	$[ReO(C_{20}H_{18}O_2N_4)Cl]$	Two molecules of CO_2
IV	50–304	9.7 (9.51)	304	–	8.14	$[ReO(H_2L)(SCN)]$	Two molecules of HCl
	304–384	21.3 (20.97)	364	–	12.40	$[ReO(C_{20}H_{18}O_2N_4)(SCN)]$	Two molecules of CO_2

H_2L^{2-}=The dianionic ligand, due to dissociation of two hydrogen ions of the NH groups.

TABLE V Antimicrobial and antifungal activities of the investigated compounds*

Compound	*Diameter of inhibition zone* (mm)		
	Aspergillus fumigatus (Fungus)	*Alternaria alternata (Fungus)*	*Bacillus cereus (Bacteria)*
Control (DMF)	5.0	7.0	14.0
H_4L	14.0	17.0	25.0
I	13.0	22.0	19.0
II	7.0	13.0	13.0
III	15.0	25.0	28.0
IV	0.0	14.0	9.0
V	16.0	26.0	23.0
VI	12.0	18.0	18.0
VII	19.0	33.0	37.0
VIII	0.0	22.0	16.0

*Values presented for the compounds are those substracted from the control values.

Magnetic Moments

The oxo complexes of rhenium(V) are all diamagnetic [25,36,42]. The magnetic moments of the mono and binuclear oxorhenium(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 : 2, 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 ^{1}H-NMR spectra of the macrocyclic ligand (H_4L) and its oxorhenium(V) complexes are listed in Table III. The free ligand (H_4L) showed a signal at δ 14.20 ppm (2H) due to carboxylic protons, broad signals at δ 7.80–8.06 ppm (2H) of the amide protons, and δ 2.09 ppm (4H) of CH_2 (alkylacetate).

In all Complexes (**I**–**IV**), the signal corresponding to the carboxylic protons and the signal of CH_2 (alkylacetate) are slightly shifted downfield or upfield from the free ligand (H_4L). The signal corresponding to the amide protons is shifted downfield (8.45–8.48) due to strong deshielding by the metal cation.

Thus the ^{1}H-NMR and IR spectra suggest that the mode of coordination of ligand (H_4L) is through the nitrogen atoms of the ring, as a neutral tetradentate ligand, consistent with the previous work on other tetraazamacrocyclic ligands with transition metal cations [43,44].

Mass Spectra

The mass spectral data are consistent with the formulations $C_{22}H_{20}O_6N_4$ (**H_4L**), $[ReO(H_4L)Cl)Cl_2$ (**II**), $[ReO(H_4L)(SCN)]Cl_2$ (**IV**), and $[ReO(H_2L)(PPh_3)]Cl$ (**VII**), which give parent ions at *m/e* 437 a.m.u. (calculated value 436.42 a.m.u.), 745.34 a.m.u. (calculated value 744.99 a.m.u.), 768.05 a.m.u. (calculated value 767.62 a.m.u.), and 935.12 a.m.u. (calculated value 934.36 a.m.u.), respectively.

The mass spectrum of the free ligand (**H_4L**), shows the presence of a mass fragment corresponding to $C_{20}H_{20}O_2N_4^+$, *m/e* 348.50 (22.02%) which is formed through loss of $2CO_2$ molecules, followed by the loss of 2CO molecules to give the fragment $C_{18}H_{20}N_4^+$, *m/e* 292.65 (18.03%). The loss of $2CH_3$ groups leads to the fragment $C_{16}H_{14}N_4^+$, *m/e* 262.75 (11.56%), and there is a fragment corresponding to $C_5H_3^+$ at *m/e* 63.00 (30.22%).

Complex **II** shows the presence of mass fragments corresponding to $ReO(H_4L)Cl_2^+$, *m/e* 709.87 (14.25%) and $ReO(H_2L)Cl^+$, *m/e* 672.75 (66.67%). The first fragment loses $2CO_2$ molecules to give the fragment $ReO(C_{20}H_{20}O_2N_4)Cl_2^+$, *m/e* 622.04 (19.54%) then loses $2Cl^\bullet$ to give the fragment $ReO(C_{20}H_{20}O_2N_4)^+$, *m/e* 550.36 (38.33%) and finally the fragment due to ReO^+ at *m/e* 202.43 (27.42%). The second fragment, $ReO(H_2L)Cl^+$, *m/e* 672.75 (66.67%), loses a Cl atom to give $ReO(H_2L)^+$, *m/e* 637.08 (8.64%), then loses $2CO_2$ molecules to give the fragment $ReO(C_{20}H_{18}O_2N_4)^+$, *m/e* 549.04 (15.32%), followed by the loss of 2CO molecules then $2CH_3$ groups and finally the fragment due to ReO^+ at *m/e* 202.43 (27.42%).

The mass spectrum of Complex **IV**, shows the presence of a mass fragment corresponding to $ReO(H_4L)(SCN)Cl^+$, *m/e* 732.43 (14.72%), which loses $2CO_2$ molecules to give the fragment $ReO(C_{20}H_{20}O_2N_4)(SCN)Cl^+$, *m/e* 644.52 (19.78%), then loses a chloride radical to give the cationic radical $ReO(C_{20}H_{20}O_2N_4)(SCN)$, *m/e* 609.08 (23.48%), followed by loss of 2CO molecules, $2CH_3$ and an HSCN molecule to give the fragment $ReO(C_{16}H_{13}N_4)^+$, *m/e* 463.54 (34.20%) and finally ReO^+, *m/e* 202.62 (24.44%).

The heated product **VII**, shows the presence of a mass fragment corresponding to $ReO(H_2L)(PPh_3)^+$, *m/e* 899.74 (35.04%), which loses $2CO_2$ molecules to give the fragment $ReO(C_{20}H_{18}O_2N_4)(PPh_3)^+$, *m/e* 811.52 (48.16%), followed by loss of 2CO molecules to give the fragment $ReO(C_{18}H_{18}N_4)(PPh_3)^+$, *m/e* 755.64 (12.36%), then loss of PPh_3 to give the fragment $ReO(C_{18}H_{18}N_4)^+$, *m/e* 492.56 (17.04%) and finally the fragment due to ReO^+ is present at *m/e* 202.54 (26.24%).

Thermal Analyses

The results of TG–DSC analyses of the complexes are shown in Table IV. All complexes are anhydrous. Complexes **I–IV** lose HCl molecules at 353, 305, 227, and 304°C, respectively. The loss of HCl molecules was accompanied by an endothermic peak with ΔH, 4.33, 31.80, 17.70, and 8.14 J/g, respectively, which led to isolable complexes (see Table IV).

The elimination of CO_2 molecules occurred at a relatively high temperature $> 364°C$, while the loss of HCl molecules occurred in the range 227–353°C. HCl molecules were eliminated from chloride ions and the protons of the NH groups of the ligand H_4L, thus the ligand changes to the dianion $(H_2L)^{2-}$.

Complex **III** loses a PPh_3 molecule at 308°C accompanied by an exothermic peak with ΔH, -12.70 J/g. This exothermic process may be due to chloride transfer from the outer to inner sphere of the complex.

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

New solid oxorhenium(V) complexes were prepared pyrolytically from the original Complexes **I–IV**. A certain amount of the original complex was placed in a porcelain crucible and heated in an oven to a fixed temperature, as indicated from the thermal analysis. The material was heated for 1/2 h, placed in a desiccator until it cooled to room temperature and then weighed. The previous steps were repeated till it reached a constant weight. Structures of the obtained products are discussed on the basis of elemental analyses, conductance, IR and electronic absorption spectra, magnetic moments and ^{1}H-NMR measurements as well as mass spectrometry (Tables I–III).

The UV-visible spectra of the heated products of the oxorhenium(V) complexes **V**–**VIII**, show four bands at 267–289, 327–337, 360–363, and 419–438 nm. The spectra of the heated products are similar to those of the initial complexes.

The magnetic moments of the heated products of the oxorhenium(V) complexes, Table III, confirm their diamagnetic character.

Pyrolytic Preparation of [$Re_2O_3(H_2L)_2$] (V)

This compound was prepared by heating 0.5 g of Complex **I** to 353°C till a constant weight 0.44 g (88%). The color of the complex was black and differed from the brown color of the mother complex.

$$\underset{\textbf{I}}{Re_2O_3(H_4L)_2]Cl_4} \xrightarrow{353^\circ C} \underset{\textbf{V}}{[Re_2O_3(H_2L)_2]} + 4HCl$$

The IR spectrum of **V** showed bands assigned to νRe=O at 914 cm^{-1} and νRe–O–Re at 714 cm^{-1}, which indicate that the complex is dinuclear, these bonds are similar to those previously cited in the literature for dinuclear complexes [22,29,38]. Bands at 1573 and 1507 cm^{-1}, due to νC=N, and at 469 and 433 cm^{-1}, due to νRe–N were also present. The νNH in the mother complexes disappeared in the heated products, due to dissociation of the protons of the NH groups. This was also supported by disappearance of the signal due to δ NH (8.47 ppm) in the ^{1}H-NMR spectrum of the mother complex, which indicates that the ligand behaves as a dianionic tetradentate ligand.

The elemental analysis and the conductivity measurement of its DMF solution indicated that the heated product is a nonelectrolyte and thus the chloride ions were lost.

From the previous results and the elemental analyses, Table I, the product obtained on heating can be represented as [$Re_2O_3(H_2L)_2$] and its proposed structure is shown in Fig. 3.

Pyrolytic Preparation of [ReO(H_2L)Cl] (VI)

Complex **VI** was prepared by heating 0.5 g of Complex **II** at 305°C to a constant weight 0.4 g (80%); the color changed from brownish-violet to deep green.

$$\underset{\textbf{II}}{[ReO(H_4L)Cl]Cl_2} \xrightarrow{305^\circ C} \underset{\textbf{VI}}{[ReO(H_2L)Cl]} + 2HCl$$

The IR spectrum of **VI** showed a band assigned to νRe=O at 970 cm^{-1}, indicating that the complex is mononuclear and similar to previous results for mononuclear complexes obtained by heating [23–27,38–40]. The band due to νRe–Cl was observed at 363 cm^{-1}, indicating that the chloride remains in the inner sphere of the complex. The stretching vibration due to NH groups disappeared in the IR spectrum of the heated product. The ^{1}H-NMR of the heated product confirms disappearance of the NH signal, which indicates that the ligand behaves as a dianionic tetradentate ligand.

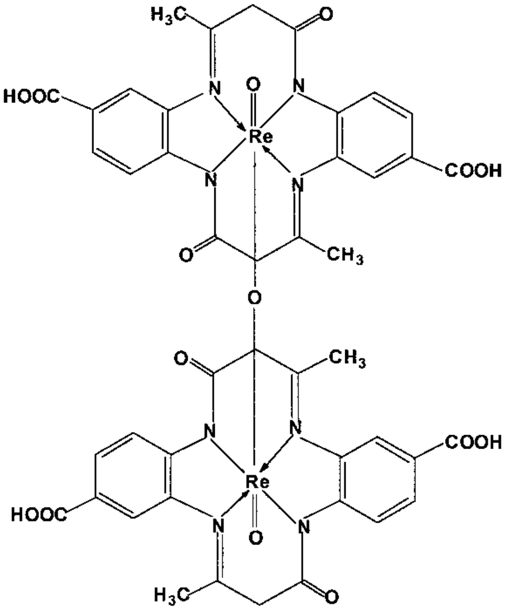


FIGURE 3 Proposed structure of $[Re_2O_3(H_2L)_2]$ (**V**), bis-8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid-μ-oxo-dioxorhenium(V) complex, obtained by heating Complex **I** to 353°C.

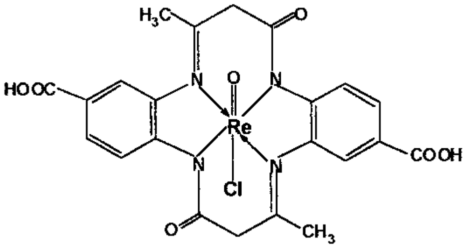


FIGURE 4 Proposed structure of $[ReO(H_2L)Cl]$ (**VI**), chloro(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid) oxorhenium(V) complex, obtained by heating Complex **II** to 305°C.

Conductivity measurements in DMF solution, showed that the heated product is a nonelectrolyte.

From the previous results and its elemental analyses, Table I, this product can be represented as $[ReO(H_2L)Cl]$ and its proposed structure is as shown in Fig. 4.

Pyrolytic Preparation of $[ReO(H_2L)(PPh_3)]Cl$ (VII)

This compound was prepared by heating 0.5 g of Complex **III** at 227°C to a constant weight 0.46 g (92%).

The color of the complex is greenish-gray differing from the greenish brown color of the mother complex.

$$\underset{\textbf{III}}{[ReO(H_4L)(PPh_3)]Cl_3} \xrightarrow{227^\circ C} \underset{\textbf{VII}}{[ReO(H_2L)(PPh_3)]Cl} + 2HCl$$

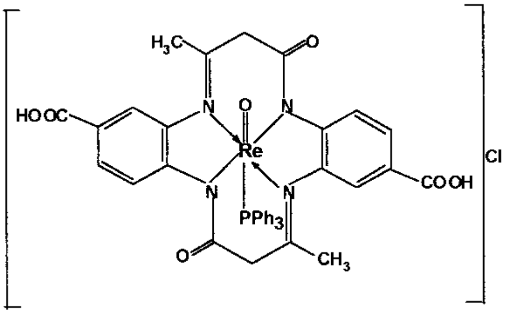


FIGURE 5 Proposed structure of [ReO(H_2L)(PPh_3)]Cl (**VII**), triphenylphosphine(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid oxorhenium(V) chloride complex, obtained by heating Complex **III** to 227°C.

The IR spectrum of **VII** showed only one band at 972 cm^{-1} due to νRe=O, which indicates that the complex is mononuclear [23–27, 38–40]. The νNH disappeared in the heated product, as did the δ NH signal in its ^{1}H-NMR spectrum.

The mass spectral data for the heated product (**VII**) showed the parent ion at *m*/*e* 935.12 (calculated value 934.36 a.m.u.) and from the elemental analysis (Table I) and conductivity measurements (Table III), this product may be represented as [ReO(H_2L)(PPh_3)]Cl (**VII**) and its proposed structure is as shown in Fig. 5.

Pyrolytic Preparation of [ReO(H_2L)(SCN)] (VIII)

This compound was also prepared by heating 0.5 g of Complex **IV** at 304°C to a constant weight 0.45 g (90%); the color changed from pale pink to deep brown.

$$\underset{\textbf{IV}}{[\mathrm{ReO(H_4L)(SCN)]Cl_2}} \xrightarrow{304^\circ\mathrm{C}} \underset{\textbf{VII}}{[\mathrm{ReO(H_2L)(SCN)]}} + 2\mathrm{HCl}$$

Its IR spectrum showed a band assigned to νRe=O at 969 cm^{-1}, which indicates that the complex is mononuclear [23–27, 38–40]. The νNH disappeared in the heated product and the elemental analysis showed the absence of chloride ions, which supports the dissociation of the protons of the NH groups in the form of HCl molecules. The ligand behaves in this case as dianionic tetradentate. The ^{1}H-NMR measurement also confirm the disappearance of the NH groups.

The band corresponding to νSCN appears at 2057 cm^{-1}, indicting that the thiocyanate anion is still coordinated via sulfur [22–26, 39]. The conductance of a DMF solution of this product proves that it is a nonelectrolyte.

From the previous results, this product can be represented as [ReO(H_2L)(SCN)] and its proposed structure is as shown in Fig. 6.

ANTIMICROBIAL ACTIVITIES

The screening of antibacterial and antifungal activities for the investigated compounds was performed using the disc diffusion method [45,46] as follows: filter paper discs

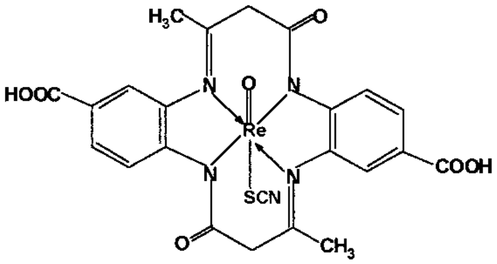


FIGURE 6 Proposed structure of $[ReO(H_2L)(SCN)]$ (**VIII**), thiocyanato (8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[a,h][14] annulene-2,11-dicarboxylic acid) oxorhenium(V) complex, obtained by heating Complex **IV** to 305°C.

(2.5 mm in diameter) were impregnated with 100 ppm of each compound dissolved in DMF, which was used as a control. Individual discs were placed aseptically on the surface of nutrient agar medium seeded with *Bacillus cereus* and incubated at 37°C for 48 h in the case of antibacterial tests and on the surface of Waksman's agar medium seeded with *Aspergillus fumigatus* or *Alternaria alternata* and incubated at 30°C for seven days in the case of antifungal tests. The diameter of inhibition zone in each case was measured and the results are presented in Table V. The tested compounds showed variable degrees of inhibition. Generally higher antifungal activities are observed against *A. alternata* than against *A. fumigatus*. Complexes **IV** and **VIII** showed no effect against *A. fumigatus*, perhaps due to the presence of an SCN group in the structure of each complex. The high activities of the heated product **V**–**VIII**, in comparison to the mother complexes may be due to elimination of the protons of the NH groups and the decrease of chloride ions in the complexes. Also, the complexes showed different antibacterial activities, some were quite low (**II** and **IV**) and others were quite high (**III** and **VII**).

CONCLUSION

The tetraaza macrocyclic ligand H_4L reacts with oxorhenium(V) complex, $H_2[ReOCl_5]$ in 6 N HCl solution to give the dinuclear Complex **I** when the concentration of HCl was decreased to 2 N, while the mononuclear Complex **II** is obtained at its ordinary concentration, 6 N. The mixed ligand oxorhenium(V) Complexes **III** and **IV** were obtained when the tetraaza macrocyclic ligand was mixed either with PPh_3 or NaSCN in 6 N HCl solution, respectively.

The structures of the obtained complexes indicated that the tetraaza macrocyclic ligand is neutral tetradentate through its four nitrogen atoms of the macrocyclic ring, while the carboxylic groups are not involved in coordinating the central rhenium ion. Both PPh_3 and SCN behave as monodentate ligands via the phosphorus and the sulfur atoms, respectively.

Thermal studies on Complexes **I**–**IV** revealed the possibility of obtaining other solid complexes by heating to certain temperatures. However, these new thermal complexes cannot be prepared directly in solution from the starting ligand and the oxorhenium(V) complex. The tetraaza macrocyclic ligand was coordinated to the central rhenium ion in products **V**–**VIII** and is dianionic tetradentate$(H_2L)^{2-}$. The ligand loses the hydrogen atoms of its NH groups at relatively high temperatures, i.e. above ~227°C.

The carboxylic groups are still uncoordinated to the rhenium ion, while at relatively high temperatures, i.e., above ~360°C, decarboxylation may occur.

Acknowledgment

The author wishes to express his thanks to Dr. Usama Fahmy Ali Hamed, Biology Department, Faculty of Education, Ain Shams University for evaluating the biological experiment.

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