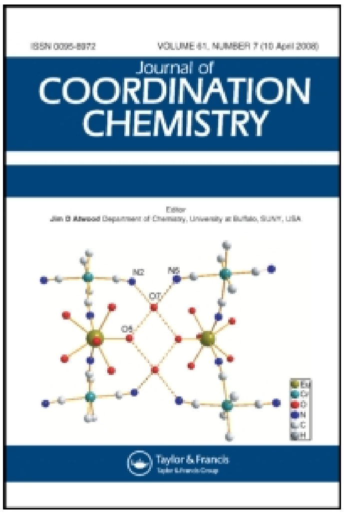

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses and structural transformations of oxorhenium(V) complexes with triazine and imidazole derivatives: mixed ligand complexes with thiocyanate, 8-hydroxyquinoline and 1,10-phenanthroline

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To cite this Article Mashaly, Mahmoud M. , Ismail, Tarek M. , El-Maraghy, Salah B. and Habib, Hesham A.(2003) 'Syntheses and structural transformations of oxorhenium(V) complexes with triazine and imidazole derivatives: mixed ligand complexes with thiocyanate, 8-hydroxyquinoline and 1,10-phenanthroline', Journal of Coordination Chemistry, 56: 15, 1307 — 1327

To link to this Article: DOI: 10.1080/00958970310001629082
URL: http://dx.doi.org/10.1080/00958970310001629082

J. Coord. Chem. Vol. 56, No. 15, 15 October 2003, pp. 1307–1327

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SYNTHESES AND STRUCTURAL TRANSFORMATIONS OF OXORHENIUM(V) COMPLEXES WITH TRIAZINE AND IMIDAZOLE DERIVATIVES: MIXED LIGAND COMPLEXES WITH THIOCYANATE, 8-HYDROXYQUINOLINE AND 1,10-PHENANTHROLINE

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(Received 11 March 2003; In final form 24 September 2003)

Mononuclear oxorhenium(V) complexes [ReO(HL^1 or H_2L^2)(PPh_3)(OH_2)Cl]Cl, {H_2L^1 = 1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone) and H_3L^2 = 1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)}, have been synthesized by ligand exchange with *trans*-trichloromonooxo-bis(triphenylphosphine) rhenium(V). The reaction of a 1 : 1 mixture of either NH_4SCN, 1,10-phenanthroline (1,10-phen) or 8-hydroxyquinoline (8-OHquin) and H_2L^1 or H_3L^2, with *trans*-$ReOCl_3(PPh_3)_2$ yielded the mononuclear oxorhenium(V) complexes, [ReO(HL^1 or H_2L^2)(PPh_3)(SCN)Cl], [ReO(HL^1)(1,10-phen)Cl]Cl, [ReO(H_2L^2)(1,10-phen)(OH_2)]$Cl_2 \cdot H_2O$ and [ReO(HL^1 or H_2L^2)(8-Oquin)Cl]. Thermal studies on these complexes showed structural transformations from mononuclear into binuclear complexes. [Re_2O_3(HL^1 or H_2L^2)$_2$(PPh_3)$_2Cl_2$], [Re_2O_2(μ-L^1 or L^2)$_2$(SCN)$_2$] and [Re_2O_3(H_2L^2)$_2$(1,10-phen)$_2$]Cl_2, were synthesized pyrolytically in the solid state from the respective precursor rhenium complexes. The structures of all complexes and the corresponding thermal products were elucidated using elemental analyses, conductance, IR and electronic absorption spectra, magnetic moments and ^{1}H NMR and TG-DSC measurements. The prepared complexes and their thermal products have octahedral configurations. The ligands H_2L^1 or H_3L^2 behave as monoanionic bidentate or monoanionic tetradentate ligands towards the oxorhenium ions. The antifungal activities of the metal complexes towards *Alternaria alternata* and *Aspergillus niger* were tested and showed comparable behavior with well known antibiotics.

Keywords: Oxorhenium; Triazine imidazole; Antifungal; Hydrazone ligands

INTRODUCTION

The chemistry of Re/Tc with 3-hydroxy-4-pyrones, a family of monoanionic bidentate O-donor ligands, has been studied [1,2]. These anionic O-donor ligands stabilize M^V with an oxo or nitrido core but their $M^{III/IV}$ complexes are ill defined, probably because of their reactivity in air and water. It is evident that these ligands alone are unable to

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ISSN 0095-8972 print: ISSN 1029-0389 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/00958970310001629082

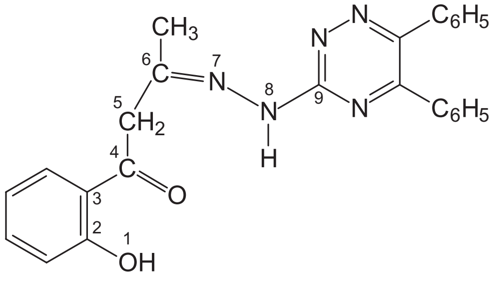
stabilize the metal center. However, this inability is an attractive feature for a "secondary ligand" in a ternary complex; it would not displace the anchoring ligand. An added advantage of these ligands is that they are easily functionalized, providing the possibility of a wealth of bioconjugation chemistry [3–8].

There is extensive literature on rhenium complexes with N-donor ligands [9–17]. With appropriate halides or oxygen donor ligands, the complexes are usually cationic and stable (or inert) in air and water in the oxidation states III, IV and V. Because N-donors are mostly neutral, their complexes commonly react with anionic oxygen donor ligands to form ternary complexes. The chemistry of ReL complexes (L = N-donor ligands) is rich and a number of chemical reactions have applications in nuclear medicine.

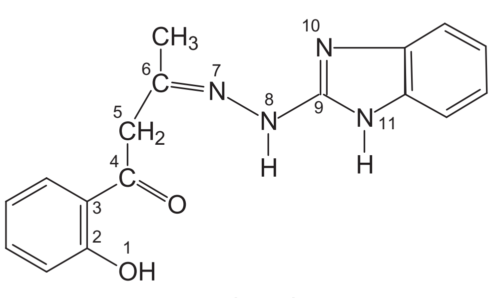
^{188}Re sulfide has been used for treatment of transplanted human liver carcinoma in Nude Mice [18]. $[^{186}Re/^{188}ReO(MAG_3)]^{2-}$ (MAG_3 = pentaanionic form of mercaptoacetyltriglycine in which the mercapto, amide and carboxyl groups are deprotonated) has been conjugated with antibodies and investigated for detection and therapy of cancer [19,20].

Benzimidazole and triazine derivatives have anti-inflammatory activity [21–24] and other biological activities [25–28] such as antibacterial, antiviral and anthelmintic. Thus the possibility exists of designing rhenium complexes with particular biological properties.

Herein we report the synthesis and characterization of 1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone), (H_2L^1) and 1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone), (H_3L^2) (Fig. 1) as OO-donor



(H_2L^1)



(H_3L^2)

FIGURE 1 1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone), (H_2L^1) and 1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone), (H_3L^2).

ligands, and also OONN-donors in their pyrolytic products. The mixed ligands NH_4SCN, 1,10-phenanthroline and 8-hydroxyquinoline were used as S, NN and NO donor ligands, respectively. Thermal studies explored the possibility of synthesizing new rhenium(V) complexes through structural transformations.

EXPERIMENTAL

The starting rhenium complex, *trans*-$ReOCl_3(PPh_3)_2$, 2-hydroxyphenyl-butane-1,3-dione, 2-hydrazinobenzimidazole and 3-hydrazino-5,6-diphenyl-1,2,4-triazine were prepared by literature methods [29–32]. NH_4SCN, 1,10-phen and 8-OHquin were BDH products. Ethanol, DMF, 1,4-dioxane, diethyl ether and DMSO were reagent grade.

Preparation of H_2L^1, 1-(2-Hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone), and H_3L^2, 1-(2-Hydroxyphenyl)butane-1,3-dione-3-(1H-benzimidazol-2-ylhydrazone)

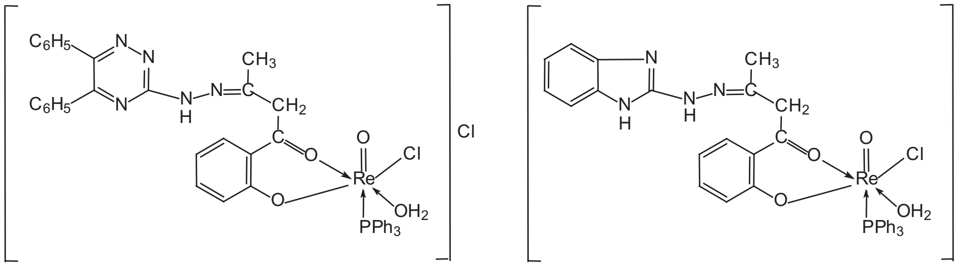
A mixture of 2-hydroxyphenyl-butane-1,3-dione (1.78 g, 10 mmol) and 3-hydrazino-5,6-diphenyl-1,2,4-triazine (2.63 g 10 mmol) or 2-hydrazinobenzimidazole (1.48 g 10 mmol) in absolute ethanol (50 cm^3) was refluxed for 1 h. An orange solid of the organic ligand H_2L^1 or a pale-brown solid of the organic ligand H_3L^2 precipitated. The isolated products were crystallized from 50% (v/v) ethanol–water; yields were 2.75 g (65%) and 2.19 g (71%), respectively.

Preparation of the Rhenium Complexes

The proposed structures of the complexes are shown in Figs. 2–5.

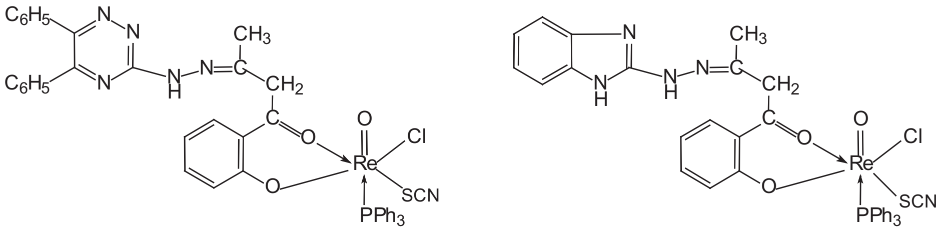
Binary Complexes, Molar Ratio M : H_2L^1 or H_3L^2, 1 : 1

*$[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$ (**1**) and $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$* (**5**) 2 g (2.4 mmol) of *trans*-$ReOCl_3(PPh_3)_2$ in 150 cm^3 of ethanol was added gradually to 1.02 g (2.4 mmol) of the ligand (H_2L^1) or 0.74 g (2.4 mmol) of the ligand (H_3L^2) dissolved in 50 cm^3 of ethanol. The reaction mixture was stirred at room temperature for 10 h, then stored for two days at the same temperature. The resulting precipitate



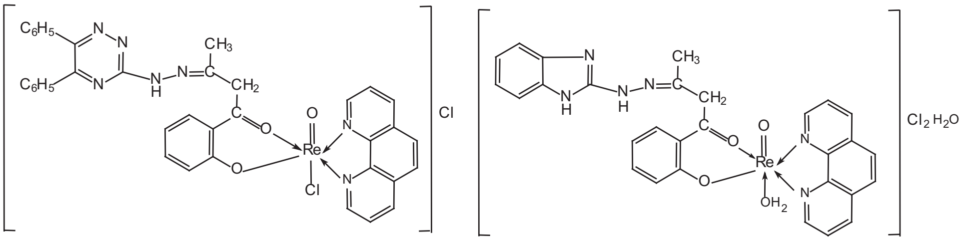
(1) **(5)**

FIGURE 2 Proposed structures of the binary oxorhenium(V) complexes: (**1**) aquochlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone)oxorhenium(V)chloride complex; (**5**) aquochlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)oxorhenium(V)chloride complex.



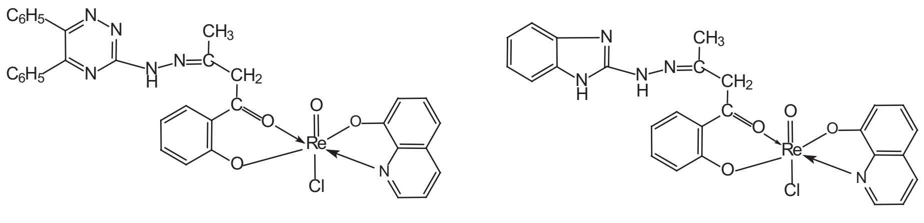
(2) **(6)**

FIGURE 3 Proposed structures of the mixed thiocyanate oxorhenium(V) complexes: (**2**) chlorothiocyanatotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone) oxorhenium(V) complex; (**6**) chlorothiocyanatotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)oxorhenium(V) complex.



(3) **(7)**

FIGURE 4 Proposed structures of the mixed 1,10-phenanthroline oxorhenium(V) complexes: (**3**) chloro-1,10-phenanthrolino-1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone) oxorhenium(V)chloride complex; (**7**) aquo-1,10-phenanthrolino-1-(2-hydroxy-phenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)oxorhenium(V)chloride complex.



(4) **(8)**

FIGURE 5 Proposed structures of the mixed 8-hydroxyquinoline oxorhenium(V) complexes: (**4**) chloro-8-hydroxyquinolino-1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone) oxorhenium(V) complex; (**8**) chloro-8-hydroxyquinolino-1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)oxorhenium(V) complex.

was filtered, washed several times with 50% (v/v) ethanol–water then with ether. Finally, the complexes were dried in a vacuum desiccator over anhydrous $CaCl_2$. The isolated yields were 1.64 g (70%) and 1.43 g (69%), respectively.

Mixed Thiocyanate Complexes, Molar Ratio $M : H_2L^1$ *or* $H_3L^2 : SCN^-$*, 1 : 1 : 1*

*$[ReO(HL^1)(PPh_3)(SCN)Cl]$ (**2**) and $[ReO(H_2L^2)(PPh_3)(SCN)Cl]$ (**6**)* 2 g (2.4 mmol) of *trans*-$ReOCl_3(PPh_3)_2$ in 150 cm^3 of ethanol was added gradually to a

mixture of 0.18 g (2.4 mmol) of NH_4SCN and 1.02 g (2.4 mmol) of the ligand (H_2L^1) or 0.74 g (2.4 mmol) of the ligand (H_3L^2) dissolved in 50 cm^3 of ethanol. The reaction mixture was stirred at room temperature for 9 h, then stored for two days at the same temperature. The resulting precipitate was filtered, washed several times with 50% (v/v) ethanol–water then with ether. Finally, the complexes were dried in a vacuum desiccator over anhydrous $CaCl_2$. The isolated products were 1.25 g (53%) and 1.10 g (53%), respectively.

Mixed 1,10-Phenanthroline Complexes, Molar Ratio M : H_2L^1 or H_3L^2 : 1,10-phen, 1 : 1 : 1

*[ReO(HL^1)(1,10-phen)Cl]Cl (**3**) and [ReO(H_2L^2)(1,10-phen)(OH_2)Cl]Cl · H_2O (7)* 2 g (2.4 mmol) of *trans*-$ReOCl_3(PPh_3)_2$ in 150 cm^3 of ethanol was added gradually to a mixture of 0.48 g (2.4 mmol) of 1,10-phen and 1.02 g (2.4 mmol) of the ligand (H_2L^1) or 0.74 g (2.4 mmol) of the ligand (H_3L^2) dissolved in 50 cm^3 of ethanol. The reaction mixture was stirred at room temperature for 9 h, then stored for two days at the same temperature. The resulting precipitate was filtered, washed several times with 50% (v/v) ethanol–water then with ether. Finally, the complexes were dried in a vacuum desiccator over anhydrous $CaCl_2$. The isolated products were 1.16 g (55%) and 1.00 g (52%), respectively.

Mixed 8-hydroxyquinoline Complexes, Molar Ratio M : H_2L^1 or H_3L^2 : 8-OHquin, 1 : 1 : 1

*[ReO(HL^1)(8-Oquin)Cl] (**4**) and [ReO(H_2L^2)(8-Oquin)Cl] (**8**)* 2 g (2.4 mmol) of *trans*-$ReOCl_3(PPh_3)_2$ in 150 cm^3 of ethanol was added gradually to a mixture of 0.35 g (2.4 mmol) of 8-OHquin and 1.02 g (2.4 mmol) of the ligand (H_2L^1) or 0.74 g (2.4 mmol) of the ligand (H_3L^2) dissolved in 50 cm^3 of ethanol. The reaction mixture was stirred at room temperature for 10 h, then stored for two days at the same temperature. The resulting precipitate was filtered, washed several times with 50% (v/v) ethanol–water then with ether. Finally, the complexes were dried in a vacuum desiccator over anhydrous $CaCl_2$. The isolated products were 1.10 g (57%) and 0.87 g (53%), respectively.

Solubilities and Antifungal Activities

Complexes **1**–**8** were soluble in DMF and DMSO and insoluble in 1,4-dioxane and ether. The complexes were partially soluble in ethanol. Table I indicates the colors, percentage yield and elemental analysis data of the ligands H_2L^1 and H_3L^2 and their oxorhenium(V) complexes.

Screening of the investigated compounds for antifungal activities was performed using the disc diffusion method [33,34] as follows: filter paper discs (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 Waksman's agar medium seeded with *Alternaria alternata* or *Aspergillus niger* and incubated at 30°C for seven days. The diameter of the inhibition zone was measured.

TABLE I Elemental analyses of the ligands H_2L^1 and H_3L^2 and their oxorhenium (V) complexes

Compound	*F.W.*	*Color*	*Yield* (%)	*Elemental Analysis Found (Calcd.)* (%)						
				C	*H*	*N*	*S*	*Re*	*Cl*	*P*
H_2L^1 $C_{25}H_{21}N_5O_2$	423.47	Orange	65	70.80	4.80	16.30	–	–	–	–
				(70.91)	(5.00)	(16.54)	–	–	–	–
(**1**) $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$	975.89	Dark greenish blue	70	52.64	3.95	7.10	–	19.20	7.10	3.00
$C_{43}H_{37}N_5O_4Cl_2PRe$				(52.92)	(3.82)	(7.18)	–	(19.08)	(7.26)	(3.17)
(**2**) $[ReO(HL^1)(PPh_3)(SCN)Cl]$	980.50	Dark violet	53	53.83	3.69	8.50	3.00	18.80	3.70	3.10
$C_{44}H_{35}N_6O_3ClPSRe$				(53.90)	(3.60)	(8.57)	(3.27)	(18.99)	(3.61)	(3.16)
(**3**) $[ReO(HL^1)(1,10\text{-phen})Cl]Cl$	875.79	Greenish blue	55	51.10	3.18	11.00	–	21.20	8.20	–
$C_{37}H_{28}N_7O_3Cl_2Re$				(50.74)	(3.22)	(11.20)	–	(21.26)	(8.10)	–
(**4**) $[ReO(HL^1)(8\text{-Oquin})Cl]$	804.28	Greenish blue	57	50.60	3.40	10.30	–	23.20	4.50	–
$C_{34}H_{26}N_6O_4ClRe$				(50.77)	(3.26)	(10.45)	–	(23.15)	(4.41)	–
H_3L^2 $C_{17}H_{16}N_4O_2$	308.34	Pale brown	71	66.30	5.00	18.10	–	–	–	–
				(66.22)	(5.23)	(18.17)	–	–	–	–
(**5**) $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$	860.75	Pale green	69	48.48	3.91	6.40	–	21.60	8.30	3.45
$C_{35}H_{32}N_4O_4Cl_2PRe$				(48.84)	(3.75)	(6.51)	–	(21.63)	(8.24)	(3.60)
(**6**) $[ReO(H_2L^2)(PPh_3)(SCN)Cl]$	865.37	Leafy green	53	49.70	3.45	7.80	3.55	21.40	4.15	3.30
$C_{36}H_{30}N_5O_3ClPSRe$				(49.97)	(3.49)	(8.09)	(3.70)	(21.52)	(4.10)	(3.58)
(**7**) $[ReO(H_2L^2)(1,10\text{-phen})(OH_2)]Cl_2 \cdot H_2O$	796.68	Reddish brown	52	43.90	3.40	10.45	–	23.40	8.70	–
$C_{29}H_{27}N_6O_5Cl_2Re$				(43.72)	(3.42)	(10.55)	–	(23.37)	(8.90)	–
(**8**) $[ReO(H_2L^2)(8\text{-Oquin})Cl]$	689.14	Green	53	44.99	3.16	10.00	–	26.95	5.00	–
$C_{26}H_{21}N_5O_4ClRe$				(45.31)	(3.07)	(10.16)	–	(27.02)	(5.14)	–
(**9**) $[Re_2O_3(HL^1)_2(PPh_3)_2Cl_2]$	1860.84	Brownish black	94	55.38	3.80	7.26	–	19.87	3.70	3.20
$C_{86}H_{70}N_{10}O_7Cl_2P_2Re_2$				(55.51)	(3.79)	(7.53)	–	(20.01)	(3.81)	(3.33)
(**10**) $[Re_2O_2(\mu\text{-}L^1)_2(SCN)_2]$	1363.50	Black	68	45.60	2.90	12.30	4.58	27.22	–	–
$C_{52}H_{38}N_{12}O_6S_2Re_2$				(45.81)	(2.81)	(12.33)	(4.70)	(27.31)	–	–
(**11**) $[Re_2O_3(H_2L^2)_2(PPh_3)_2Cl_2]$	1630.57	Black	93	51.40	3.65	6.64	–	22.70	4.40	3.70
$C_{70}H_{60}N_8O_7Cl_2P_2Re_2$				(51.56)	(3.71)	(6.87)	–	(22.84)	(4.35)	(3.80)
(**12**) $[Re_2O_2(\mu\text{-}HL^2)_2(SCN)_2]$	1133.23	Black	64	38.02	2.60	12.23	5.52	32.90	–	–
$C_{36}H_{28}N_{10}O_6S_2Re_2$				(38.15)	(2.49)	(12.36)	(5.66)	(32.86)	–	–
(**13**) $[Re_2O_3(H_2L^2)_2(1,10\text{-phen})_2]Cl_2$	1466.40	Black	91	47.38	3.07	11.25	–	25.34	4.90	–
$C_{58}H_{46}N_{12}O_7Cl_2Re_2$				(47.51)	(3.16)	(11.46)	–	(25.40)	(4.83)	–

Physical Measurements and Analyses

TG-DSC measurements were carried out on a SHIMADZU thermogravimetric analyzer in dry nitrogen with a heating rate of 10 deg/min using the TA-50 WSI program. ^1H NMR spectra (DMSO-d_6) were recorded at room temperature on a cryomagnet for NMR spectroscopy, 200 MHz/52MM, a product of Spectrospin and Bruker, using TMS as an internal standard. 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 calibrant. 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 and polystyrene as a calibrant. Far-IR spectra were measured with a Nicolet 20F-FTIR spectrophotometer using polyethylene discs. Conductivities were measured for solutions of the complexes in DMF (1×10^{-3}M) using a Model LBR 40A, conductivity meter (Wissenschaftlich-Techmische Werkstatten, D 8120 Weilheim, Germany). 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 nitron-perrhenate and silver chloride, respectively [35].

RESULTS AND DISCUSSION

The reactions of *trans*-$ReOCl_3(PPh_3)_2$ with the ligand 1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone), (H_2L^1) or 1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone), (H_3L^2) in ethanolic solutions (95%) and at room temperature yielded the mononuclear complexes **1** and **5**, respectively, Fig. 2. The reaction of a 1 : 1 mixture of NH_4SCN, 1,10-phen or 8-OHquin and H_2L^1 or H_3L^2, with *trans*-$ReOCl_3(PPh_3)_2$ in ethanolic solutions (95%) yielded mononuclear oxorhenium(V) complexes **2** and **6** (Fig. 3) **3** and **7** (Fig. 4) and **4** and **8** (Fig. 5), respectively.

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

IR Spectra

The IR spectra of the free ligands H_2L^1 and H_3L^2 and their complexes are listed in Table II. The IR spectra of the free ligands H_2L^1 and H_3L^2 show characteristic bands for $\nu(OH)^1$ at 3449 and 3419 cm^{-1}, respectively. In all complexes, the stretching vibrations due to OH^1 groups disappear, indicating that these groups are involved in coordinating the metal cation.

$\nu(C{=}O)$ of the free ligands H_2L^1 and H_3L^2 was observed at 1705 and 1687 cm^{-1}, respectively, and shifted (34–48cm^{-1}) to lower frequencies in complexes, owing to the participation of the carbonyl groups in coordination.

The IR spectra of the free ligands H_2L^1 and H_3L^2 show characteristic bands for $\nu(NH^8)$ at 3125 and 3165 cm^{-1}, respectively, $\nu(C{=}N^7)$ at 1584 and 1581 cm^{-1}, respectively, and $\nu(C{=}N)$ (ring) at 1535 and 1514 cm^{-1}, respectively; in addition, $\nu(NH)$ (ring) was observed in the free ligand H_3L^2 at 3117 cm^{-1}. In all complexes **1**–**8**, these bands were unaffected, which indicates that these groups are not involved in coordinating the metal cation.

TABLE II Characteristic IR bands (cm^{-1}) of the ligands H_2L^1 and H_3L^2 and their oxorhenium(V) complexes

Compound	*νOH¹*	*νNH⁸*	*νNH (ring)*	*νCH (aromatic)*	*νCH (aliphatic)*	*νSCN*	*νC=O*	*νC=N⁷, νC=N (ring)*	*νRe=O*	*νRe–Cl*	*νRe–P*	*Additional bands*
H_2L^1 $C_{25}H_{21}N_5O_2$	3449br	3125s	–	3055s	2975s, 2901s	–	1705m	1584m, 1535s	–	–	–	–
1	–	3128m	–	3056s	2968m, 2924s	–	1662m	1588m, 1530s	997s	359m	312m	3508br (coordinated water), 684m, 637 w, 617m ν(Re–O)
2	–	3127m	–	3056s	2970m, 2925s	2067s	1661m	1587s, 1528m	996s	367m	310m	639 w, 618m ν(Re–O), 288m ν(Re–S)
3	–	3129m	–	3056s	2964m, 2925s	–	1657m	1582s, 1527m	998s	364m	–	1547s (coordinated C=N of 1,10-phen), 643 w, 618m ν(Re–O), 459m ν(Re–N)
4	–	3127m	–	3057s	2958m, 2924s	–	1659m	1580s, 1526m	967s	368m	–	1548m (coordinated C=N of 8-OHquin), 638m, 617 w, 597m ν(Re–O), 432m ν(Re–N)
H_3L^2 $C_{17}H_{16}N_4O_2$	3419br	3156m	3117m	3055s	2987m, 2883s	–	1687m	1581m, 1514s	–	–	–	–
5	–	3159m	3119m	3055s	2967m, 2924s	–	1651m	1580m, 1516s	997s	365m	310m	3502br (coordinated water), 693s, 637 w, 619m ν(Re–O)
6	–	3157m	3118m	3058s	2969m, 2925m	2065s	1650m	1584m, 1516m	997s	368m	311m	693s, 620m ν(Re–O), 293m ν(Re–S)

7	–	3159m	3120m	3057s	2972m, 2924s	–	1653m	1582m, 1517m	994s	–	–	3505br (coordinated water), 3376br (lattice water), 1549s (coordinated C=N of 1,10-phen), 693s, 639w, 618m ν(Re–O), 456m ν(Re–N)
8	–	3159m	3118m	3059s	2986m, 2925s	–	1651m	1580m, 1518m	998s	366m	–	1569s (coordinated C=N of 8-OHquin), 694s, 634m, 597m ν(Re–O), 467m ν(Re–N)
9	–	3129m	–	3058s	2967m, 2926s	–	1658m	1585m, 1532s	912s	368m	314m	715m ν_{as}(Re–O–Re), 684m, 639m ν(Re–O)
10	–	–	–	3056s	2972m, 2924s	2064s	1659m	1554m, 1530s	917s	–	–	647m, 619m ν(Re–O), 468m, 433m ν(Re–N), 286 ν(Re–S)
11	–	3154m	3116m	3057s	2970m, 2922s	–	1653m	1582m, 1514s	910s	367m	308m	712m ν_{as}(Re–O–Re), 690s, 634m ν(Re–O)
12	–	–	3118m	3055s	2966m, 2927s	2062s	1657m	1559m, 1518m	916s	–	–	690s, 627m ν(Re–O), 456m, 432m ν(Re–N), 292 w ν(Re–S)
13	–	3155m	3117m	3059s	2976m, 2920m	–	1556m	1580m, 1520m	917s	–	–	1553s (coordinated C=N of 1,10-phen), 716s ν_{as}(Re–O–Re), 692s, 633m ν(Re–O), 458m ν(Re–N)

s = strong; m = medium; w = weak; br = broad.

TABLE III Physico-chemical measurements of the ligands H_2L^1 and H_3L^2 and the initial Re(V) complex and their oxorhenium(V) complexes

Compound	*Molar conductance*[a] ($ohm^{-1} cm^2 mol^{-1}$)	μ_{eff}[b] (*B.M.*)	λ_{max}[a] (nm)	δ^c *OH*^{1}	δ^c *NH*^{8}	δ^c *NH*^{11}	δ^c *CH*$_2^5$	*Additional bands*
$[ReOCl_3(PPh_3)_2]$	–	–	286, 411, 481	–	–	–	–	–
H_2L^1 $C_{25}H_{21}N_5O_2$	–	–	288, 306, 348	15.21 (1H)	10.09 (1H)	–	2.52 (2H)	–
1	54	0.07	243, 295, 324, 346, 597	–	10.08 (1H)	–	2.52 (2H)	δ 3.45 (2H) coordinated water
2	9	0.05	247, 290, 301, 355, 586	–	10.12 (1H)	–	2.54 (2H)	–
3	48	0.11	222, 284, 304, 353, 601	–	10.10 (1H)	–	2.52 (2H)	–
4	7	0.09	220, 283, 298, 384, 605	–	10.14 (1H)	–	2.52 (2H)	–
H_3L^2 $C_{17}H_{16}N_4O_2$	–	–	293, 307, 355	15.07 (1H)	9.87 (1H)	9.46 (1H)	2.52 (2H)	–
5	45	0.06	288, 307, 380, 530	–	9.80 (1H)	9.48 (1H)	2.52 (2H)	δ 3.46 (2H) coordinated water
6	10	0.09	284, 312, 351, 536	–	9.84 (1H)	9.44 (1H)	2.52 (2H)	–
7	97	0.05	283, 312, 385, 579	–	9.85 (1H)	9.46 (1H)	2.52 (2H)	δ 2.97 (2H) lattice water, δ 3.49 (2H) coordinated water
8	9	0.09	287, 311, 389, 398	–	9.92 (1H)	9.49 (1H)	2.50 (2H)	–
9	7	0.05	246, 292, 322, 351, 600	–	10.04 (2H)	–	2.54 (4H)	–
10	6	0.06	245, 287, 303, 376, 564	–	–	–	2.52 (4H)	–
11	11	0.06	284, 305, 403, 582	–	9.82 (2H)	9.44 (2H)	2.54 (4H)	–
12	6	0.09	269, 301, 400, 560	–	–	9.47 (2H)	2.56 (4H)	–
13	94	0.04	278, 314, 392, 602	–	9.86 (2H)	9.44 (2H)	2.52 (4H)	–

[a] DMF Solutions, 1×10^{-3}M, at 26°C.

[b] Measurements were taken at 27°C.

[c] Chemical shifts with reference to TMS.

TABLE IV Thermal analysis data for the oxorhenium (V) complexes

Compound	*Temperature range* (°C)	*Loss in weight Expl.* (%) (*Calcd.*)	*DSC peak* (°C)		ΔH (J/g)	*Composition of residue*	*Probable composition of expelled groups*
			Endo	*Exo*			
1	100–192	4.69 (4.66)	–	192	−34.78	$[Re_2O_3(HL^1)_2(PPh_3)_2Cl_2]$	One molecule of coordinated water and two molecules of HCl from two complex molecules
	192–538	60.80 (60.51)	–	388	−4.96	$[Re_2O_3(C_{10}H_9NO_2)_2]$	Two molecules of HCl, two molecules of PPh_3, and two molecules of $(C_6H_5)_2C_3N_4$ from two complex molecules
2	100–346	30.72 (30.47)	–	346	−74.36	$[Re_2O_2(\mu\text{-}L^1)_2(SCN)_2]$	Two molecules of HCl and two molecules of PPh_3 from two complex molecules
	346–463	49.12 (48.95)	408	–	14.33	$[Re_2O_2(C_{35}H_{28}N_6O_4)]$	One molecule of $(SCN)_2$ and one molecule of $(C_6H_5)_2C_3N_4$ from two complex molecules
3	120–368	36.59 (36.45)	–	200	−58.51	$[ReO(C_{10}H_9NO_2)(1,10\text{-phen})]$	Two molecules of HCl and one molecule of $(C_6H_5)_2C_3N_4$
	368–522	57.23 (56.99)	405	–	3.99	$[ReO(C_{10}H_9NO_2)]$	One molecule of 1,10-phen.
4	125–461	35.28 (35.15)	436	–	9.79	$[ReO(C_{10}H_9NO_2)(8\text{-Oquin})]$	One molecule of HCl and one molecule of $(C_6H_5)_2C_3N_4$
	461–537	53.32 (53.08)	485	–	4.40	$[ReO(C_{10}H_9NO_2)]$	One molecule of 8-Oquin.
5	50–206	5.34 (5.28)	–	206	−21.44	$[Re_2O_3(H_2L^2)_2(PPh_3)_2Cl_2]$	One molecule of coordinated water and two molecules of HCl from two complex molecules
	206–359	40.26 (39.99)	331	–	12.95	$[Re_2O_3(HL^2)_2]$	Two molecules of HCl and two molecules of PPh_3 from two complex molecules
	359–458	55.43 (55.22)	448	–	7.00	$[Re_2O_3(C_{10}H_9NO_2)_2]$	Two molecules of $C_7H_5N_3$ from two complex molecules
6	120–318	34.64 (34.52)	–	318	−48.35	$[Re_2O_2(\mu\text{-}HL^2)_2(SCN)_2]$	Two molecules of HCl and two molecules of PPh_3 from two complex molecules
	318–422	56.47 (56.39)	344	–	4.87	$[Re_2O_2(C_{10}H_9NO_2)_2]$	One molecule of $(SCN)_2$ and two molecules of $C_7H_5N_3$ from two complex molecules
7	34–94	2.29 (2.26)	78	–	83.65	$[ReO(H_2L^2)(1,10\text{-phen})(OH_2)]Cl_2$	One molecule of lattice water
	94–236	8.06 (7.97)	–	236	−22.44	$[Re_2O_3(H_2L^2)_2(1,10\text{-phen})_2]Cl_2$	One molecule of coordinated water and two molecules of HCl from two complex molecules
	236–364	29.23 (29.01)	–	303	−277.45	$[Re_2O_3(C_{10}H_9NO_2)_2(1,10\text{-phen})_2]$	Two molecules of HCl and two molecules of $C_7H_5N_3$ from two complex molecules
	364–558	61.87 (61.60)	442	–	4.24	$[Re_2O_3(C_{10}H_9NO_2)_2]$	Two molecules of 1,10-phen from two complex molecules
8	70–339	24.47 (24.32)	255	–	3.81	$[ReO(C_{10}H_9NO_2)(8\text{-Oquin})]$	One molecule of HCl and one molecule of $C_7H_5N_3$
	339–559	45.43 (45.24)	379	–	12.87	$[ReO(C_{10}H_9NO_2)]$	One molecule of 8-Oquin.

ν(Re=O) bands of the mother complexes **1**–**8** occur between 967–998 cm^{-1}, consistent with the value cited in the literature for similar mononuclear complexes [36–44].

The IR spectra of the mixed thiocyanate complexes **2** and **6**, (Fig. 3), showed a new strong band at 2067 and 2065 cm^{-1}, respectively, which indicate coordination of the SCN group to the rhenium cation via the sulfur atom [45–49]. The Re–S stretching frequencies appear at low frequency, 288 and 293 cm^{-1} [50–53], respectively.

The mixed 1,10-phenanthroline complexes **3** and **7** (Fig. 4) showed a new band at 1547 and 1549 cm^{-1}, respectively, which is due to the coordinated C=N group of 1,10-phenanthroline [54–56].

The mixed 8-hydroxyquinoline complexes **4** and **8** (Fig. 5) did not show a band at ~3300 cm^{-1} due to the deprotonation of the OH group of 8-OHquin, while new bands were observed at 1548 and 1569 cm^{-1}, respectively, assigned to the coordinated C=N group of 8-hydroxyquinoline [40].

Complex **7** showed a band at 3376 cm^{-1}, due to the stretching vibration of the lattice water molecule, while the coordinated water molecules were observed at 3508, 3502 and 3505 cm^{-1} for complexes **1**, **5** and **7**, respectively. The mononuclear complexes **1**, **2**, **5** and **6** show new bands at 310–312 cm^{-1}due to ν(Re–P) [57,58], which confirm the coordination of PPh_3 in the inner sphere of the complex.

Stretching vibrations ν(Re–O), ν(Re–N) and ν(Re–Cl) were observed at 597–694, 432–467 and 359–368 cm^{-1}, respectively.

UV-Visible Spectra

Electronic absorption spectra are summarized in Table III. The UV-Vis spectra of the free ligands H_2L^1 and H_3L^2 show three absorption bands at 286–293, 306–307 and 348–355 nm. The prepared rhenium complexes of H_2L^1 show five absorption bands at 220–247, 283–295, 298–324, 346–384 and 586–605 nm, while the rhenium complexes of H_3L^2 show four bands at 283–288, 307–312, 351–389 and 530–598 nm. The bands observed in the visible range are consistent with ligand field electronic transitions, $n\text{d} \rightarrow \sigma^*\text{d}$ and $n\text{d} \rightarrow \pi^*\text{d}$ usually observed for metal complexes with the 4–5d^2 electronic configuration [57,59].

Magnetic Moments

The oxo complexes of rhenium(V) are all diamagnetic [60–62]. The magnetic moments of all oxorhenium(V) complexes, Table III, confirm their diamagnetic character.

Conductivity Measurements

Conductivity measurements, Table III, showed that complexes **1**, **3** and **5** are 1 : 1 electrolytes, while complex **7** is a 1:2 electrolyte. Complexes **2**, **4**, **6** and **8** are non-electrolytes. The relatively low values of the measured conductivities may be due to the bulky cations which contain the Re=O(V) ion.

NMR Spectral Studies

The assignment of the main signals in the ^{1}H NMR spectra of the organic ligands H_2L^1 and H_3L^2 and their oxorhenium(V) complexes are listed in Table III. The free ligands

H_2L^1 and H_3L^2 showed signals at δ 15.21(1H) and 15.07(1H), respectively, due to the OH^1 group. The spectra of the free ligands showed signals at δ 10.09(1H), δ 9.87(1H) and δ 9.46(1H). The first and the second signals are assigned to the proton of the NH^8 group of H_2L^1 and H_3L^2, respectively, while the third signal is assigned due to the NH^{11} group of ligand H_3L^2. The protons of methylene group (CH_2^5) were observed at δ 2.52(2H) for both ligands.

In all the complexes the signal corresponding to the OH^1 group disappeared, indicating the deprotonation of the phenolic OH group during formation of the metal complexes.

The signals due to the NH^8 or NH^{11} groups do not undergo significant chemical shifts, because they are not involved in coordinating the metal cation. Also, the signal due to the methylene group (CH_2^5) was unaffected in all complexes.

The mixed 8-OHquin complexes **4** and **8** do not show a signal due to the OH group of 8-OHquin at ~13 ppm, which indicates the deprotonation of this group during the formation of these complexes.

Complexes **1**, **5** and **7** showed a resonance due to coordinated water molecules in the range 3.45–3.49 ppm, while the resonance due to lattice water was observed at δ 2.97(2H) for complex **7**.

From both ^1H NMR and IR spectra, we suggest that the organic ligands H_2L^1 and H_3L^2 are coordinated as monoanionic bidentate ligands through the oxygen atoms of the OH^1 and the carbonyl groups.

Thermal Analyses

The results of TG-DSC analyses of the binary and mixed ligand complexes are shown in Table IV. The results are consistent with the theoretical formulae as suggested from the analytical data, Table I.

All complexes are anhydrous except complex **7**, which loses its lattice water molecule at 94°C. This process is accompanied by an endothermic peak at 78°C, $\Delta H = 83.65$ J/g.

Elimination of coordinated water molecules was accompanied by loss of HCl in complexes **1**, **5** and **7**. This process leads to structural transformations from mononuclear into binuclear complexes and has enabled us to isolate complexes **9**, **11** and **13** at 192, 206 and 236°C, respectively.

The mixed 1,10-phen complex **3** loses two molecules of HCl and one molecule of $(C_6H_5)_2C_3N_4$ at 386°C accompanied by an exothermic peak at 200°C ($\Delta H = -58.51$ J/g). This process leads to a non-isolable complex.

The mixed thiocyanate complexes **2** and **6** lose two molecules of HCl and two molecules of PPh_3 in one step at 346 and 318°C, respectively. This step leads to structural transformations from mononuclear to binuclear complexes and is accompanied by an exothermic peak at 346 ($\Delta H = -74.36$ J/g) for **2** and at 318°C ($\Delta H = -48.35$ J/g) for **6**. HCl molecules are formed from chloride ions and protons from the NH^8 group of the coordinated monoanionic bidentate ligand (HL^1 or H_2L^2) converting them to bridged dianionic tridentate ligands towards rhenium(V) ions and giving rise to isolable complexes **10** and **12**.

The mixed 1,10-phen and 8-OHquin complexes lose the 1,10-phen and 8-Oquin molecules at temperatures > 520 and > 530°C, respectively, leading to non-isolable complexes.

Pyrolytic Preparation of some Rhenium(V) Complexes and their Characterization

New solid oxorhenium(V) complexes were prepared pyrolytically from complexes **1**, **2**, **5**, **6** and **7**. A certain amount of the mother 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 30 min, then placed in a desiccator to cool to room temperature and weighed. The previous steps were repeated to constant weight. Structures of the obtained products are discussed on the basis of their elemental analyses, conductance, IR and electronic absorption spectra, magnetic moments and ^{1}H NMR measurements (Tables I–III).

The UV-Vis spectra of the heated products of the oxorhenium(V) complexes **9** and **10** show five absorption bands at 245–246, 287–292, 303–322, 351–376 and 564–600 nm while the spectra of complexes **11**–**13**, show four absorption bands at 269–284, 301–314, 392–403 and 560–602 nm. The spectra of the heated products are more or less similar to those of the mother complexes.

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

Pyrolytic Preparation of [$Re_2O_3(HL^1)_2(PPh_3)_2Cl_2$] (9)

This compound was prepared by heating 0.5 g of complex **1** at 192°C to constant weight, yield 0.47 g (94%). The complex was brownish black, different from the dark greenish-blue of complex **1**.

$$\underset{\mathbf{1}}{2[\mathrm{ReO(HL^1)(PPh_3)(OH_2)Cl]Cl}} \xrightarrow{192^\circ\mathrm{C}} \underset{\mathbf{9}}{[\mathrm{Re_2O_3(HL^1)_2(PPh_3)_2Cl_2}]} + 2\mathrm{HCl} + \mathrm{H_2O}$$

The IR spectrum showed bands assigned to ν(Re=O) at 912 cm^{-1} and ν(Re–O–Re) at 715 cm^{-1}, which indicates the structural transformation into a binuclear complex [9,49–52]. The stretching vibration due to the coordinated water molecule in the mother complex disappeared in **9**.

The other IR bands observed in the spectrum of complex **9** were similar to those for complex **1**, indicating that the mode of coordination of the ligand (H_2L^1) was unaffected.

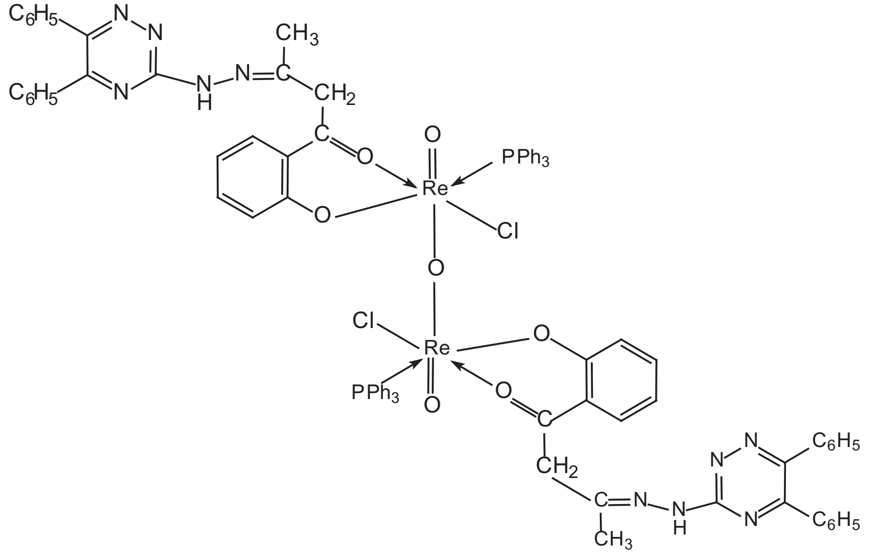
The ^{1}H NMR data support the results of IR spectra. The signal due to the coordinated water molecule δ 3.45(2H) in the spectrum of the mother complex disappeared in complex **9**.

Elemental analysis and conductivity measurements of a DMF solution of complex **9** indicate a non-electrolyte. From the previous results and the elemental analyses (Table I), the product obtained on heating can be represented as [$Re_2O_3(HL^1)_2(PPh_3)_2Cl_2$] (9) and its proposed structure is shown in Fig. 6.

Pyrolytic Preparation of [$Re_2O_2(\mu\text{-}L^1)_2(SCN)_2$] (10)

Upon heating 0.5 g of complex **2** at 346°C to constant weight, yield 0.32 g (68%), the color changed from dark violet to black.

$$\underset{\mathbf{2}}{2[\mathrm{ReO(HL^1)(PPh_3)(SCN)Cl}]} \xrightarrow{346^\circ\mathrm{C}} \underset{\mathbf{10}}{[\mathrm{Re_2O_2(\mu{-}L^1)_2(SCN)_2}]} + 2\mathrm{HCl} + 2\mathrm{PPh_3}$$



(9)

FIGURE 6 Proposed structure of $[Re_2O_3(HL^1)_2(PPh_3)_2Cl_2]$ (**9**), bis-1-(2-hydroxyphenyl)butane-1,3- dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone)dichloro-bis-triphenylphosphine-μ-oxo-dioxodirhenium(V) complex, obtained by heating complex **1** at 192°C.

The IR spectrum of complex **10** showed the disappearance of the $\nu(NH^8)$, ν(Re–P) and ν(Re–Cl) bands. New bands are observed at 468 and $433\,cm^{-1}$, assigned to ν(Re–N) [49,51,53]. The Re=O stretching frequency was observed at $917\,cm^{-1}$, indicating a binuclear complex [9,53,63]. The ν(Re–O–Re) band was not observed.

The $\nu(C{=}N^7)$ band was shifted to lower frequency, which indicates the participation of the $C{=}N^7$ group in coordination, in addition to the nitrogen atom of NH^8 group, which acts as a bridge between the two rhenium ions. The remaining IR bands for **10** were the same as for complex **2**.

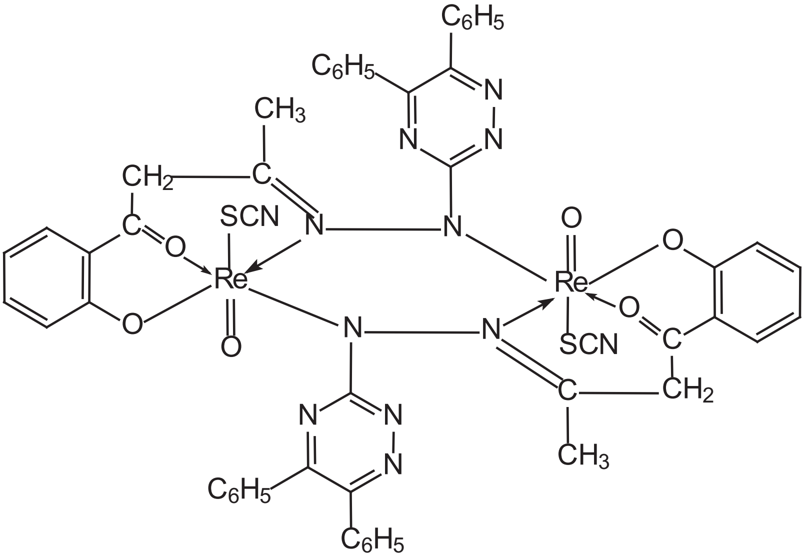
The ^1H NMR spectrum of **10** confirms the disappearance of the signal due to the NH^8 group, which indicates that the ligand behaves as a dianionic tetradentate ligand. Conductivity measurements in DMF solution proved that complex **10** is a non-electrolyte.

From the previous results and its elemental analyses, Table I, the product obtained on heating can be represented as $[Re_2O_2(\mu\text{-}L^1)_2(SCN)_2]$ (**10**) and its proposed structure is shown in Fig. 7.

Pyrolytic Preparation of $[Re_2O_3(H_2L^2)_2(PPh_3)_2Cl_2]$ (11)

This compound was prepared by heating 0.5 g of complex **5** at 206°C to constant weight, yield 0.46 g (93%). The color of the complex is black, different from the pale-green of complex **5**.

$$\underset{\mathbf{5}}{2[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl} \xrightarrow{206^\circ C} \underset{\mathbf{11}}{[Re_2O_3(H_2L^2)_2(PPh_3)_2Cl_2]} + 2HCl + H_2O$$



(10)

FIGURE 7 Proposed structure of $[Re_2O_2(\mu\text{-}L^1)_2(SCN)_2]$ (**10**), dithiocyanate-(-bis-1-(2-hydroxyphenyl) butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone) dioxodirhenium(V) complex, obtained by heating complex **2** at 346°C.

The IR spectrum of **11** showed bands at 910 and 712 cm^{-1}, assigned to ν(Re=O) and ν(Re–O–Re), respectively, indicating a binuclear complex [9,49–52]. The stretching vibration due to the coordinated water molecule disappeared in the heated product. The other IR bands observed in the heated product were similar to those in the mother complex, indicating that the mode of coordination of the ligand (H_3L^2) was unaffected. Also, ^1H NMR spectrum data support the IR results. The resonance due to coordinated H_2O δ(3.46 ppm) is absent in complex **11**. The conductance of a DMF solution of this product proved that it is a non-electrolyte.

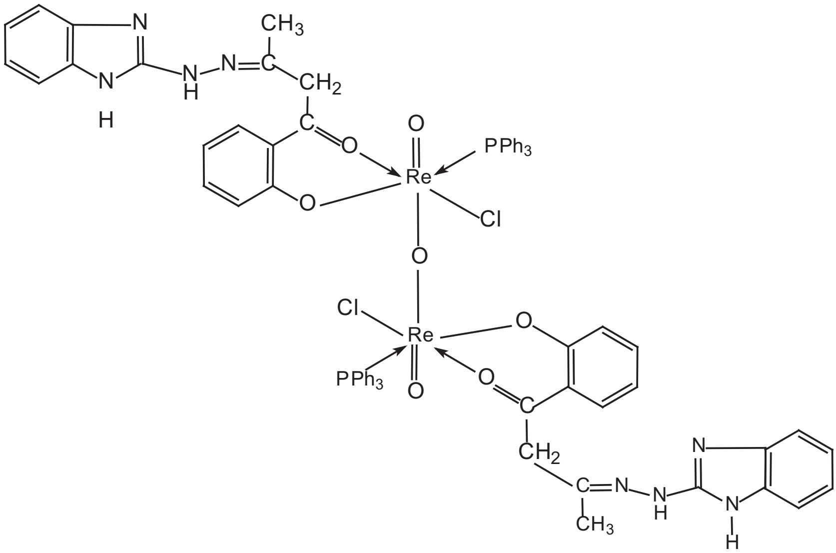
From the previous results and its elemental analyses (Table I), the product can be represented as $[Re_2O_3(H_2L^2)_2(PPh_3)_2Cl_2]$ **(11)**, and its proposed structure is shown in Fig. 8.

Pyrolytic Preparation of $[Re_2O_2(\mu\text{-}HL^2)_2(SCN)_2]$ *(12)*

Upon heating 0.5 g of complex **6** at 318°C to constant weight, yield 0.32 g (64%), the color changed from leaf green to black.

$$\underset{\mathbf{6}}{2[ReO(H_2L^2)(PPh_3)(SCN)Cl]} \xrightarrow{318^\circ C} \underset{\mathbf{12}}{[Re_2O_2(\mu{-}HL^2)_2(SCN)_2]} + 2HCl + 2PPh_3$$

The IR spectrum of complex **12** showed a band assigned to ν(Re=O) at 917 cm^{-1}, similar to that observed in binuclear complexes [9,53,63]. The band due to ν(Re–O–Re) was not observed. The stretching frequencies due to $\nu(NH^8)$, ν(Re–P) and



(11)

FIGURE 8 Proposed structure of [$Re_2O_3(H_2L^2)_2(PPh_3)_2Cl_2$] (**11**), bis-1-(2-hydroxyphenyl) butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)dichloro-bis-triphenylphosphine-μ-oxo-dioxodirhenium(V) complex, obtained by heating complex **5** to 206°C.

ν(Re–Cl) were absent in the spectrum of **12**. New bands are observed at 456 and 432 cm^{-1} assigned to ν(Re–N) [49,51,53].

The $\nu(C{=}N^7)$ band shifted to lower frequency, indicating participation of the $C{=}N^7$ group in coordination, in addition to the nitrogen atom of the NH^8 group, which acts as a bridge between the two rhenium ions. The remaining IR bands for **6** were the same as for **12**.

The ^1H NMR spectrum of **12** confirms the disappearance of the NH^8 signal, indicating that the ligand HL^2 behaves as a dianionic tetradentate ligand. The conductivity of its DMF solution indicates that complex **12** is a non-electrolyte.

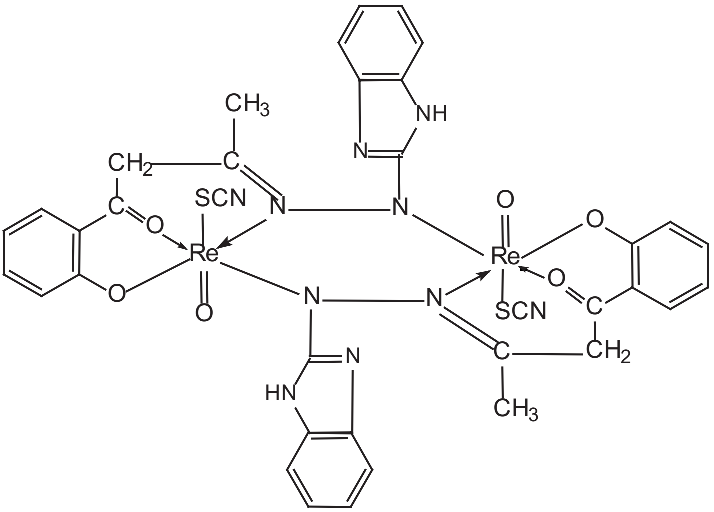
From the previous results and its elemental analyses (Table I), the product obtained on heating can be represented as [$Re_2O_2(\mu\text{-}HL^2)_2(SCN)_2$] (**12**) and its proposed structure is shown in Fig. 9.

Pyrolytic Preparation of [$Re_2O_3(H_2L^2)_2(1,10\text{-phen})_2]Cl_2$ (13)

This compound was prepared by heating 0.5 g of complex **7** at 236°C to constant weight, yield 0.45 g (91%). The complex is black, different from the reddish-brown complex **7**.

$$\underset{\mathbf{7}}{2[ReO(H_2L^2)(1,10\text{-phen})(OH_2)]Cl_2 \cdot H_2O} \xrightarrow{236^\circ C} \underset{\mathbf{13}}{[Re_2O_3(H_2L^2)_2(1,10\text{-phen})_2]Cl_2} + 2HCl + 3H_2O$$

The IR spectrum of **13** showed a new band at 716 cm^{-1} due to ν(Re–O–Re) formed through dimerization [9,49–52]. The stretching frequency of the Re=O bond also



(12)

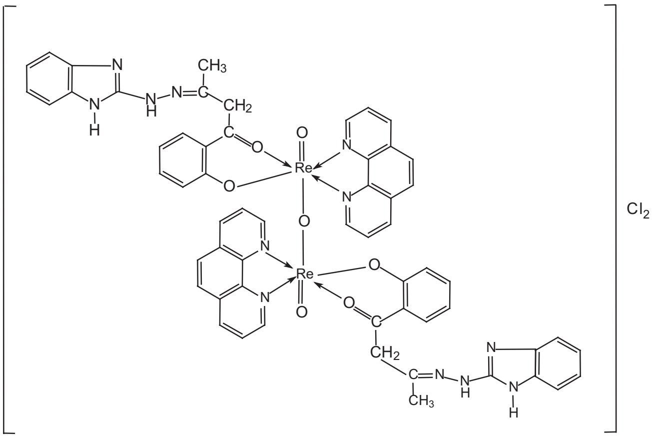
FIGURE 9 Proposed structure of [$Re_2O_2((-HL^2)_2(SCN)_2$] (**12**), dithiocyanato-μ-bis-1-(2-hydroxyphenyl)-butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone) dioxodirhenium(V) complex, obtained by heating complex **6** at 318°C.

shifted to lower frequency, 917 cm^{-1}. The spectrum showed the disappearance of the stretching frequencies due to lattice and coordinated water molecules, results supported by the ^{1}H NMR spectrum. The ν(C=N) stretching frequency of 1,10-phen was observed at ~1553 cm^{-1}, indicating that 1,10-phen is still coordinated to rhenium. The remaining IR bands for **13** are similar to those of the mother complex, indicating that the mode of coordination of the organic ligand H_2L^2 is unaffected. Conductivity measurements in DMF solution, showed that **13** is a 1:2 electrolyte.

From the previous results and its elemental analyses, Table I, the product can be represented as [$Re_2O_3(H_2L^2)_2$(1,10-phen)$_2$]Cl_2 (**13**) and its proposed structure is shown in Fig. 10.

ANTIFUNGAL ACTIVITIES

The results of antifungal activity tests of the ligands and the metal complexes are presented in Table V. The compounds show variable degrees of inhibition. All the prepared complexes **1**–**13** and the starting rhenium(V) complex, *trans*-$ReOCl_3(PPh_3)_2$ enhance the activities towards *Alternaria alternata* and *Aspergillus niger* compared to those of the free ligands. Complexes **1**–**5**, **10**, **12** and **13** showed higher activities towards both fungi than *trans*-$ReOCl_3(PPh_3)_2$, while complexes **6**–**9** and **11** and the free ligands H_2L^1 and H_3L^2 give lower activities. The mixed ligand complexes of triazine showed higher activities than those of imidazole. Some of the isolated Re(V) complexes showed antifungal effects similar to those of antibiotics and even higher in some cases (see Table VI). These results may direct more attention to the use of these complexes in medical treatments.



(13)

FIGURE 10 Proposed structure of $[Re_2O_3(H_2L^2)_2(1,10\text{-phen})_2]Cl_2$ (**13**), bis-1,10-phenanthrolino-bis-1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)-μ-oxo-dioxodirhenium(V)chloride complex, obtained by heating complex **7** at 236°C.

TABLE V Antifungal activities of the investigated compounds

Compound	*Diameter of inhibition zone* (mm)	
	Alternaria alternata	Aspergillus niger
$ReOCl_3(PPh_3)_2$	16	21
H_2L^1	7	9
H_3L^2	8	6
1	19	35
2	24	29
3	18	23
4	31	34
5	42	41
6	8	11
7	6	9
8	15	17
9	12	14
10	37	35
11	9	15
12	32	39
13	46	41

Values presented for the compounds are those subtracted from the control values.

TABLE VI Antifungal activities of some antibiotics

Antibiotic	*Diameter of inhibition zone* (mm)	
	Alternaria alternata	Aspergillus niger
Ampicillin	35	37
Ultrafen	40	43
Dalacin C	21	25
Flumox	33	29
Unasyn	19	12
Cefradine	13	16
Doxymycin	8	9
Septrin	6	7

CONCLUSION

The hydrazone ligands derived from triazine (H_2L^1) or imidazole (H_3L^2) react with *trans*-$ReOCl_3(PPh_3)_2$ in ethanolic solution to give the mononuclear complexes **1** and **4**. The reaction of a 1:1 mixture of either NH_4SCN, 1,10-phen or 8-Ohquin and H_2L^1 or H_3L^2 with *trans*-$ReOCl_3(PPh_3)_2$ in ethanolic solutions afforded the mixed ligand complexes **2**–**4** and **6**–**8**, respectively.

The mode of coordination of both the organic ligands H_2L^1 or H_3L^2 is as monoanionic bidentate ligands through oxygen atoms of the OH^1 and the carbonyl groups. The ligands NH_4SCN, 1,10-phen and 8-OHquin behave as monoanionic monodentate, neutral bidentate and monoanionic bidentate ligands, respectively.

Thermal studies on the above complexes gave structural transformations. The binuclear complexes **9**–**13** were isolated pyrolytically from the corresponding mononuclear mother complexes. The modes of coordination of the organic ligands H_2L^1 or H_3L^2 in products **10** and **12** had changed. These complexes were isolated at temperature $>300°C$ and the organic ligands behave as bridged dianionic tetradentate ligands.

Complexes **9**, **11** and **13** dimerize through an oxygen bridge. This bridge is formed via the initial formation of two hydroxyoxorhenium complexes, which lose one molecule of water to give the oxygen bridge in the dimer [53,64]. The hydroxy complexes are formed by elimination of two molecules of HCl, where the hydrogen was extracted from a water molecule already present in the mother complex. The thiocyanato complexes were devoid of hydrated or coordinated water molecules. Consequently, the bridge was formed through change in the mode of coordination of the ligands.

All the prepared complexes **1**–**13** and the starting oxorhenium(V) complex, *trans*-$ReOCl_3(PPh_3)_2$, have antifungal activities. Some of the isolated Re(V) complexes show antifungal effects similar to those of antibiotics and even higher in some cases.

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