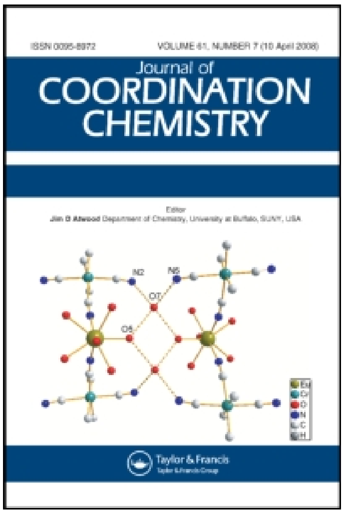

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Mahmoud M. Mashaly[a]
[a] Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt

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HETEROBINUCLEAR AND HETEROTRINUCLEAR COMPLEXES OF OXORHENIUM(V) WITH Cu(II), Ni(II), Fe(III), UO_2(VI) AND Th(IV) IN THE SOLID STATE

MAHMOUD M. MASHALY*

Department of Chemistry, Faculty of Education, Ain Shams University, Roxy, Cairo, Egypt

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New heteronuclear complexes containing oxorhenium(V), Cu(II), Ni(II), Fe(III), UO_2(VI) and Th(IV) ions were prepared by the reaction of the complex ligand, $[ReO(H_4L)Cl]Cl_2$, where $H_4L = $ 8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[*a,h*][14]annulene-2,11-dicarboxylic acid, with the previous transition and actinide salts. Three heteronuclear Cu(II) complexes were isolated depending on the ratio of $[ReO(H_4L)Cl]Cl_2 : Cu(II)$ ion. When the ratios were 1 : 0.5, 1 : 1 and 1 : 2, the heteronuclear complexes $\{[ReO(H_3L)Cl]_2CuCl_2(OH_2)_2\}SO_4 \cdot H_2O$ (**I**), $[ReO(H_3L)Cl_2Cu(OH_2)_2(SO_4)]$ (**II**) and $\{ReO(H_2L)Cl[Cu(OH_2)_3SO_4]_2\}$ (**III**) were obtained, respectively. Heteronuclear complexes of the other metal cations were obtained by mixing $[ReO(H_4L)Cl]Cl_2$ with the metal salt in the ratio 1 : 1 to obtain the heteronuclear complexes $[ReO(H_3L)Cl_2Ni(OH_2)_2](NO_3)_2$ (**IV**), $[ReO(H_3L)Cl_3Fe(OH_2)_3](NO_3)_2$ (**V**), $[ReO(H_3L)ClUO_2(NO_3)_2(OH_2)]Cl$ (**VI**) and $[ReO(H_3L)Cl_3Th(NO_3)_2(OH_2)]NO_3 \cdot 2H_2O$ (**VII**). The complex ligand coordinates with the hetero-metal ion via the carboxylate group, and the infrared bands ν_{as} COO and ν_s COO indicate that the carboxylate acts as a unidentate ligand to the heterometal cations. Cu(II) and Fe(III) cations in the heteronuclear complexes have octahedral geometry, while Ni(II) is square planar. Thermal studies explored the possibility of obtaining new heteronuclear complexes pyrolytically in the solid state from the corresponding mother complexes. The structures of the complexes were elucidated by conductance, IR and electronic spectra, magnetic moments, ^1H NMR and TG-DSC measurements as well as by mass spectroscopy.

Keywords: Oxorhenium; Copper(II); Heteronuclear

INTRODUCTION

Rhenium(V) complexes derived from 7-α-substituted estradiol were used in diagnosis and detection of breast cancer [1], rhenium complexes of substituted progesterone derivatives were used for the diagnostic imaging of steroid receptor-positive breast tumors [2]. In the area of bioinorganic chemistry, dibenzotetraaza[14]annulene complexes of the middle to late transition metals have continued to be studied as models for the active sites of certain naturally occurring enzymes. The complex $[Co(Me_4taa)]$ has been

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*Corresponding author. E-mail: mashalym@hotmail.com

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studied by Moore and coworkers because of the resemblance of the macrocyclic ligand to the corrin ring of vitamin B_{12} coenzyme [3].

Manganese (III) complexes of peripherally substituted dibenzotetraaza[14]annulenes are effective catalysts for the oxidation of certain nitroso compounds to the nitro derivatives and thus may be considered mimics of the function of the cytochrome P-450 enzymes [4]. In another area of activity, electrochemical studies of middle to late transition metal dibenzotetraaza[14]annulene complexes can lead to the synthesis of new materials [5–8].

Wilkinson and coworkers [9] prepared the mixed rhenium(V) and (VI) complexes with magnesium, $(Me_4ReO)_2Mg(thf)_4$ and $[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$ (thf = tetrahydrofuran) by reacting Grignard reagents with Re_2O_7, $[Me_3NH][ReO_4]$, $ReOCl_4$ or $ReOCl_3(PPh_3)_2$. Mixed-metallic complexes constitute an important part of modern inorganic chemistry owing to the nature of these compounds as active sites in a variety of metalloenzymes [10,11], and play a significant and expanding role in industrial catalysis [11] and materials chemistry [13–16].

Herein, we report the synthesis and characterization of a complex ligand, $[ReO(H_4L)Cl]Cl_2$, and its coordination behavior toward Cu(II), Ni(II), Fe(III), UO_2(VI) and Th(IV) ions.

EXPERIMENTAL

The complex ligand $[ReO(H_4L)Cl]Cl_2$ (Fig. 1), was prepared by a literature method [17]. $CuSO_4 \cdot 5H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $UO_2(NO_3)_2 \cdot 6H_2O$ and $Th(NO_3)_4 \cdot 5H_2O$ were purchased from BDH, Analar or Merck. Ethanol, methanol, DMF, 1,4-dioxane, acetone, chloroform, ether, DMSO and HCl were reagent grade.

Preparation of the Heteronuclear Complexes

*$\{[ReO(H_3L)Cl]_2CuCl_2(OH_2)_2\}SO_4H_2O$ (**I**)* An ethanolic solution ($40\,cm^3$) of $CuSO_4 \cdot 5H_2O$ (0.15 g, 0.60 mmol) was added to an ethanolic solution ($40\,cm^3$) of the complex ligand $[ReO(H_4L)Cl]Cl_2$ (0.89 g, 1.20 mmol). The solution was refluxed for 2 h. On cooling to room temperature, the precipitate was filtered, washed several

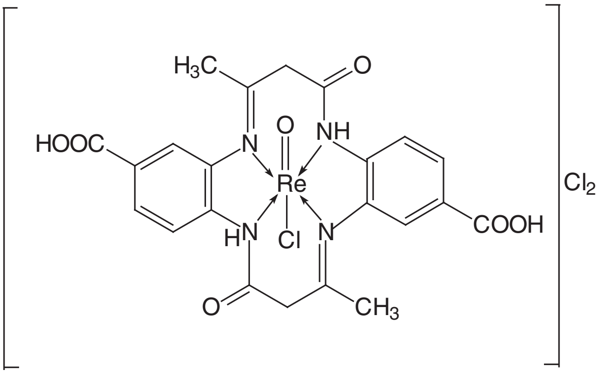


FIGURE 1 Chloro(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[*a*,*h*][14]annulene-2,11-dicarboxylic acid) oxorhenium(V) chloride, (complex ligand).

times with a mixture of 50% (v/v) ethanol–water, then ether and finally air-dried. The product isolated was 1.33 g (68%) of an olive-green solid.

*$[ReO(H_3L)Cl_2Cu(OH_2)_2SO_4]$ (**II**)* This complex was prepared similarly to complex (**I**) except that the amount of $CuSO_4 \cdot 5H_2O$ was doubled and the time of heating was 3 h. The product obtained was 0.79 g (73%) of a brown solid.

*$\{ReO(H_2L)Cl[Cu(OH_2)_3SO_4]_2\}$ (**III**)* This complex was prepared similarly to complex (**I**) except that the amount of $CuSO_4 \cdot 5H_2O$ was 0.6 g, 2.4 mmol and the time of heating was 5 h. The product isolated was 0.84 g (64%) of a pale-brown solid.

*$[ReO(H_3L)Cl_2Ni(OH_2)_2](NO_3)_2$ (**IV**)* An ethanolic solution (40 cm^3) of $Ni(NO_3)_2 \cdot 6H_2O$ (0.35 g, 1.20 mmol) was added to an ethanolic solution (40 cm^3) of the complex ligand $[ReO(H_4L)Cl]Cl_2$ (0.89 g, 1.20 mmol). The solution was refluxed for 3 h. The solution was allowed to cool to room temperature. The solid product was obtained by filtration, washed with a mixture of 50% (v/v) ethanol–water, then ether and finally air-dried. The product obtained was 0.85 g (76%) of a deep-brown solid.

*$[ReO(H_3L)Cl_3Fe(OH_2)_3](NO_3)_2$ (**V**)* An ethanolic solution (30 cm^3) of $Fe(NO_3)_3 \cdot 9H_2O$ (0.48 g, 1.20 mmol) was added to an ethanolic solution (40 cm^3) of the complex ligand $[ReO(H_4L)Cl]Cl_2$ (0.89 g, 1.20 mmol). The solution was refluxed for 2 h. On cooling to room temperature, the formed precipitate was filtered, washed several times with a mixture of 50% (v/v) ethanol–water, then ether and finally air-dried. The product obtained was 0.73 g (62%) of a pale-brown solid.

*$[ReO(H_3L)ClUO_2(NO_3)_2(OH_2)]Cl$ (**VI**)* An ethanolic solution (40 cm^3) of $UO_2(NO_3)_2 \cdot 6H_2O$ (0.60 g, 1.20 mmol) was added to an ethanolic solution (40 cm^3) of the complex ligand $[ReO(H_4L)Cl]Cl_2$ (0.89 g, 1.20 mmol), and the solution was refluxed for 4 h. The solution was allowed to cool to room temperature. The solid product was obtained by filtration, washed with a mixture of 50% (v/v) ethanol-water, then ether and finally air-dried. The product obtained was 1.02 g (76%) of a yellow solid.

*$[ReO(H_3L)Cl_3Th(NO_3)_2(OH_2)]NO_3 \cdot 2H_2O$ (**VII**)* This complex was prepared in a way similar to complex (**VI**) except that $Th(NO_3)_4 \cdot 5H_2O$ was used instead of $UO_2(NO_3)_2 \cdot 6H_2O$. The product isolated was 0.92 g (63%) of an orange-brown solid.

Complexes **I–VII** are soluble in DMF and DMSO and partially soluble in ethanol. Complexes **VI** and **VII** are partially soluble in 1,4-dioxane while complexes **I–V** are insoluble.

Physical Measurements and Analyses

Electronic spectra of the metal complexes as DMF solutions 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. 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 a calibrant. Diamagnetic corrections were calculated from Pascal's constants [18]. ^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. Mass spectra were recorded on a Hewlett-Packard mass spectrometer, model MS 5988. Analyses of metals were carried out on an optima 3000 Perkin-Elmer inductivity coupled plasma instrument (ICP). Chloride ion was determined gravimetrically as silver chloride [19]. Microanalyses of carbon, hydrogen, nitrogen and sulfur were carried out at the Microanalytical Center, Cairo University, Giza, Egypt. Conductivities were measured on solutions of the complexes in DMF (1×10^{-3} M) using a Wissenschaftlich-Techmische Werkstatten, D 8120 Weilheim, Germany, Model LBR 40A, conductivity meter. 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. The diffusion method [20–24] was used to evaluate the antibacterial activities of the tested compounds as follows:

0.5 mL spore suspension (10^6–10^7 spore/cm^3) of each of the investigated organisms was added to a sterile agar medium just before solidification, then poured into sterile Petri dishes (9 cm in diameter) and left to solidify. Using a sterile corkborer (6 mm in diameter), three holes (wells) were drilled and 0.1 cm^3 DMF solution containing 10 μg/cm^3 of each of the investigated compounds was poured into these holes. Finally the dishes were incubated at 37°C for 48 h, where clear (inhibition) zones were detected around each hole.

0.1 cm^3 DMF alone was used as a control under the same conditions. By subtracting the diameter of the inhibition zone resulting from DMF alone for each of the tested compounds, antibacterial activities can be calculated as a mean of three replicates.

RESULTS AND DISCUSSION

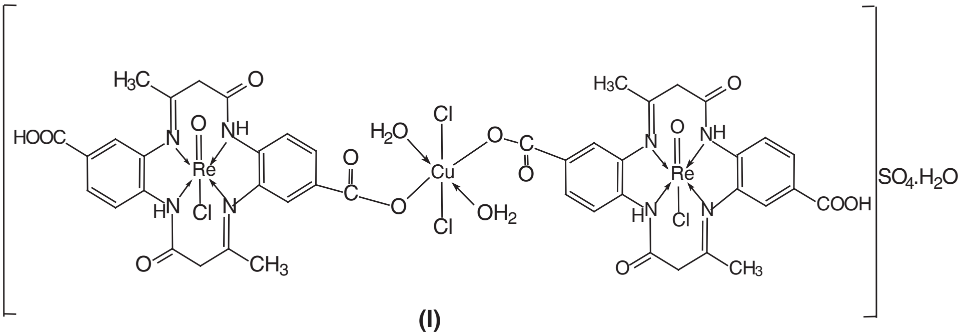
The reaction of the complex ligand $[ReO(H_4L)Cl]Cl_2$ with various metal ions produces a new series of heteronuclear complexes, $\{[ReO(H_3L)Cl]_2CuCl_2(OH_2)_2\}SO_4 \cdot H_2O$ (**I**), $[ReO(H_3L)Cl_2Cu(OH_2)_2SO_4]$ (**II**), $\{ReO(H_2L)Cl[Cu(OH_2)_3SO_4]_2\}$ (**III**), $[ReO(H_3L)Cl_2Ni(OH_2)_2](NO_3)_2$ (**IV**), $[ReO(H_3L)Cl_3Fe(OH_2)_3](NO_3)_2$ (**V**), $[ReO(H_3L)ClUO_2(NO_3)_2(OH_2)]Cl$ (**VI**) and $[ReO(H_3L)Cl_3Th(NO_3)_2(OH_2)]NO_3 \cdot 2H_2O$ (**VII**). The structures of **I**, **II** and **III** are shown in Fig. 2, those of **IV** and **V** in Fig. 3 and those of **VI** and **VII** in Fig. 4. The complexes were obtained by mixing the complex ligand and the metal ions in equal molar ratios (1 : 1), except for complexes (**I**) and (**III**) which were obtained by mixing the complex ligand and the Cu(II) ion in 1 : 0.5 or 1 : 2 molar ratios respectively.

The addition of metal salts to the complex ligand $[ReO(H_4L)Cl]Cl_2$ does not replace the oxorhenium(V) ion in the tetraaza ring, but coordination of the heterometal occurs via the terminal carboxylate groups.

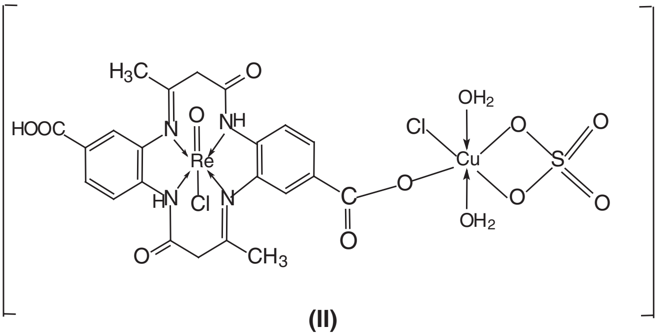
The isolated heteronuclear complexes were amorphous upon removal of the solvent. Tables I–IV contain data for the complexes.

IR Spectra

The IR spectra of the complex ligand $[ReO(H_4L)Cl]Cl_2$ and its heterometal complexes are listed in Table II. The IR spectrum of the complex ligand shows bands at 3183, 1574 and 1509 cm^{-1} due to coordinating NH and C=N groups of the tetraaza ring. These bands were unaffected in all heteronuclear complexes, which indicates that the oxorhenium(V) cation is still coordinated to the tetraaza ring.



(I)



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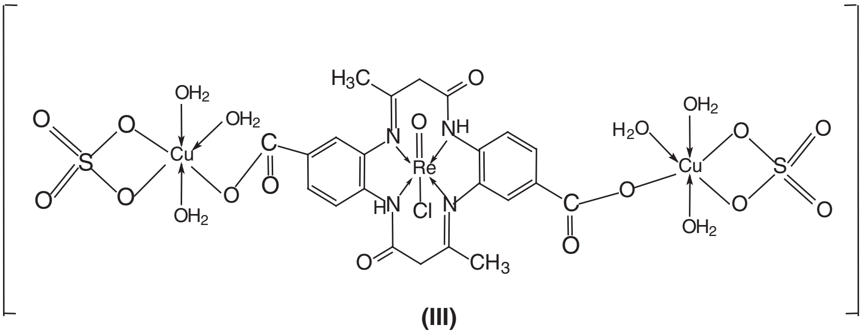
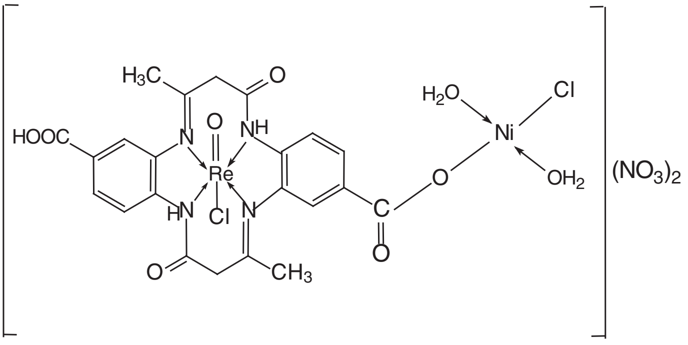


(III)

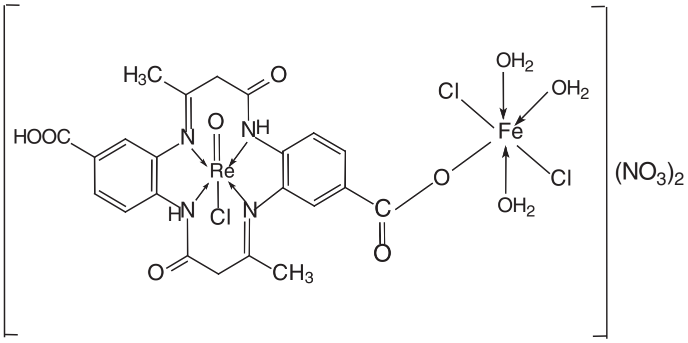
FIGURE 2 Structures of heteronuclear complexes of oxorhenium(V) and Cu(II) ion. (**I**) Diaquadichlorocopper(II) bis[chloro(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[*a*,*h*][14]annulene-2,11-dicarboxylic acid) oxorhenium(V)] sulphate hydrate; (**II**) Diaquachlorosulphatocopper(II) [chloro-(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[*a*,*h*][14]annulene-2,11-dicarboxylic acid) oxorhenium (V)]; (**III**) Bis[triaquasulphatocopper(II)] chloro(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[*a*,*h*][14]annulene-2,11-dicarboxylic acid) oxorhenium(V).

The stretching vibrations, νC=O, of the alkylacetate groups (1630 cm^{-1}) were unaffected in all complexes, indicating that these carbonyl groups are not involved in coordinating to the metal cations. The participation of the nitrogen atoms of the ring, from the NH and C=N groups, in coordinating Re(V) was also confirmed by the appearance of bands in the range 427–466 cm^{-1} attributed to νRe–N [25].

νRe=O for the mononuclear complex ligand $[ReO(H_4L)Cl]Cl_2$ observed at 969 cm^{-1} appears for all heteronuclear complexes in the range 956–966 cm^{-1}, consistent



(IV)



(V)

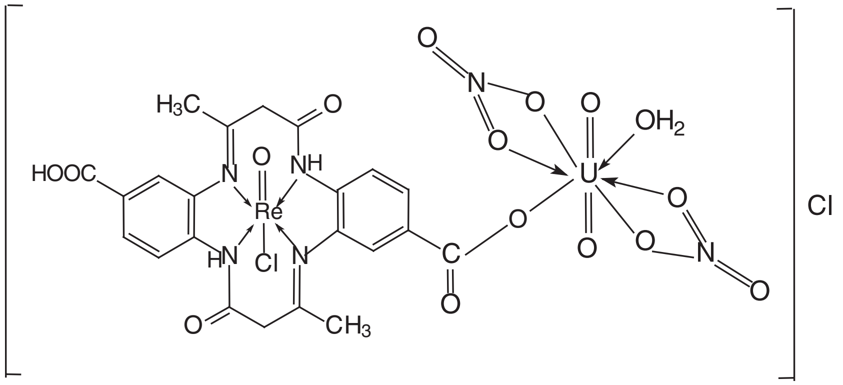
FIGURE 3 Structures of heteronuclear complexes of oxorhenium(V) and Ni(II) or Fe(III) ions. (**IV**) Diaquachloronickel(II) [chloro(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[*a*,*h*][14]annulene-2,11-dicarboxylic acid) oxorhenium(V)] nitrate; (**V**) Triaquadichloroiron(III) [chloro(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[*a*,*h*][14]annulene-2,11-dicarboxylic acid) oxorhenium(V)] nitrate.

with values previously cited in the literature for similar oxorhenium(V) complexes [26–32].

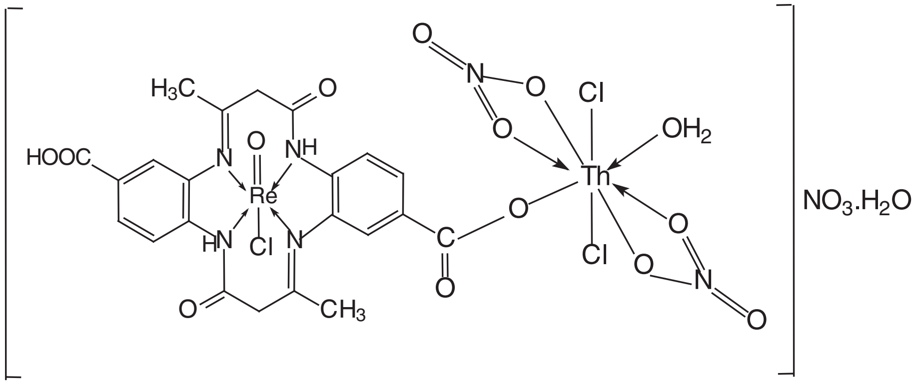
The intensity of the carbonyl group bond due to free carboxylate groups (1679 cm^{-1}) in the complex ligand decreased for the heteronuclear complexes except for complex (**III**), when the bond disappeared. A new band appeared at 1636–1643 cm^{-1}, which indicated participation of the carboxylate group in coordinating the heterometal ions. The participation of carboxylate group(s) in the heteronuclear complexes was confirmed by the appearance of two bands at 1440–1475 and 1355–1368 cm^{-1} assigned to $\nu_{as}\text{COO}^-$ and $\nu_s\text{COO}^-$ respectively, indicating that the carboxylate group acts as a unidentate group [25].

The stretching vibration of the coordinated water molecules appears at 3515–3534 cm^{-1} for heteronuclear complexes, while this band was not observed in the complex ligand. Complexes **I** and **VII** showed broad bands at 3315 and 3326 cm^{-1}, respectively, due to H-bonded lattice water molecules.

Complex **I** showed a broad band at 1118 cm^{-1} which is assigned to the ionic sulfate group, while complexes **II** and **III** showed bands at 1038–1040, 1074–1077, 1126–1132,



(VI)



(VII)

FIGURE 4 Structures of heteronuclear complexes of oxorhenium(V) and UO_2(VI) or Th(IV) ions. (**VI**) Aquadinitratodioxouranium(VI) [chloro(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[*a*,*h*][14]annulene-2,11-dicarboxylic acid) oxorhenium(V)] chloride; (**VII**) Aquadichlorodinitratothorium(IV) [chloro(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[*a*,*h*][14]annulene-2,11-dicarboxylic acid) oxorhenium(V)] nitrate dihydrate complex.

1154–1158 and 1202–1208 cm^{-1} due to bidentate chelating sulfate groups. The presence of an ionic sulfate group in complex **I** was also confirmed by addition of $BaCl_2$.

The stretching vibration of the ionic nitrate group was observed as two bands in the ranges 1380–1384 and 826–828 cm^{-1} for complexes **IV** and **V**. Bands from bidentate chelating nitrate groups in complex **VI** were observed at 1517, 1410, 1384, 1252 and 815 cm^{-1} and for complex **VII** at 1514, 1414, 1388, 1256 and 812 cm^{-1}, similar to those previously reported for bidentate nitrate groups [33].

The bands observed in the heteronuclear complexes at 356–362 cm^{-1} are assigned to νRe–Cl, while the new bands in the range 338–344 cm^{-1}, which are observed in all complexes except **III** and **VI**, may be assigned to the heterometal–chloride bonds. Also, the complexes showed new bands in the range 616–668 cm^{-1}, due to the bond between the heterometal cation and the oxygen atom. These bands were not observed in the complex ligand.

TABLE I Analytical and physical data for heteronuclear oxorhenium(V) complexes

Compound	*Mol. wt.*	*Color*	*Yield (%)*	*Elemental analyses found (calcd.) (%)*						
				C	*H*	*N*	*S*	*Re*	*M*	*Cl*
$[ReO(H_4L)Cl]Cl_2$	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)
I $\{[ReO(H_3L)Cl]_2CuCl_2(OH_2)_2\}SO_4\cdot H_2O$	1630.71	Olive-green	68	32.20	2.60	6.50	2.00	22.70	3.95	8.50
$C_{44}H_{44}N_8O_{21}SRe_2Cl_4Cu$				(32.41)	(2.72)	(6.87)	(1.96)	(22.84)	(3.89)	(8.69)
II $[ReO(H_3L)Cl_2Cu(OH_2)_2(SO_4)]$	904.16	Brown	73	29.50	2.60	6.00	3.40	20.70	7.20	7.70
$C_{22}H_{23}N_4O_{13}SReCl_2Cu$				(29.22)	(2.56)	(6.19)	(3.55)	(20.59)	(7.03)	(7.84)
III $\{ReO(H_2L)Cl[Cu(OH_2)_3SO_4]_2\}$	1099.37	Pale brown	64	23.20	2.70	5.00	5.90	17.00	11.40	3.20
$C_{22}H_{30}N_4O_{21}S_2ReClCu_2$				(24.03)	(2.75)	(5.09)	(5.83)	(16.94)	(11.56)	(3.22)
IV $[ReO(H_3L)Cl_2Ni(OH_2)_2](NO_3)_2$	927.25	Deep brown	76	28.30	2.70	8.80	–	20.20	6.10	7.60
$C_{22}H_{23}N_6O_{15}ReCl_2Ni$				(28.50)	(2.50)	(9.06)	–	(20.08)	(6.33)	(7.64)
V $[ReO(H_3L)Cl_3Fe(OH_2)_3](NO_3)_2$	977.88	Pale brown	62	26.80	2.30	8.30	–	19.00	5.50	10.80
$C_{22}H_{25}N_6O_{16}ReCl_3Fe$				(27.02)	(2.57)	(8.59)	–	(19.04)	(5.71)	(10.87)
VI $[ReO(H_3L)ClUO_2(NO_3)_2(OH_2)]Cl$	1120.58	Yellow	76	23.60	2.00	7.30	–	16.50	21.00	6.20
$C_{22}H_{21}N_6O_{16}ReCl_2U$				(23.58)	(1.89)	(7.50)	–	(16.62)	(21.24)	(6.33)
VII $[ReO(H_3L)Cl_3Th(NO_3)_2(OH_2)]\ NO_3\cdot 2H_2O$	1216.10	Orange-brown	63	21.90	2.10	7.80	–	15.30	19.20	8.80
$C_{22}H_{25}N_7O_{19}ReCl_3Th$				(21.73)	(2.07)	(8.06)	–	(15.31)	(19.08)	(8.74)

TABLE II Characteristic IR bands (cm^{-1}) of the complex ligand [ReO(H$_4$L)Cl]Cl$_2$ and its heteronuclear complexes

Compound	*νOH*	*νNH*	*νC=O*	*νC=N*	*ν_{as}COO*	*ν_sCOO*	*νRe=O*	*νM–N*	*νM–Cl*	*Additional bands*
[ReO(H$_4$L)Cl]Cl$_2$	3425br	3183br	1679s, 1630m	1574s, 1509s	–	–	969s	466m, 432m	359m	–
I	3418m	3180br	1673m, 1642s, 1628m	1572s, 1508s	1462m	1357m	956s	462m, 427m	358m, 342m	3530br (coordinated water), 3315br (lattice water), 1118br (ionic sulfate group), 637m and 616w(νCu–O)
II	3420m	3186br	1676m, 1639s, 1630m	1576s, 1508s	1475m	1368m	964s	465m, 430m	356m, 340m	3515br (coordinated water), 1040s, 1077m, 1132m, 1154sh and 1208s (bidentate chelating sulfate group), 648m, 622w, 610m (νCu–O)
III	–	3184br	1643m, 1630m	1575s, 1508s	1469m	1358m	967s	465m, 433m	357m	3526br (coordinated water), 1038s, 1074m, 1126m, 1158sh and 1202s (bidentate chelating sulfate groups), 654m, 628w, 614m (νCu–O)
IV	3422m	3181br	1678m, 1643s, 1632m	1573s, 1509s	1469m	1359m	966s	466m, 430m	360m, 338m	3522br (coordinated water), 1384s, 826w (ionic nitrate), 638m, 618w (νNi–O)
V	3426m	3180br	1676m, 1636s, 1628m	1576s, 1508s	1473m	1360m	962s	464m, 428m	362m, 343m	3535br (coordinated water), 1380s, 828w (ionic nitrate), 664m, 639m, 622w (νFe–O)
VI	3420m	3182br	1678m, 1640s, 1630m	1574s, 1509s	1440m	1355m	960s	465m, 432m	358m	3524br (coordinated water), 1517s, 1410m, 1384m, 1252s and 815 (bidentate chelating NO$_3^-$ group), 912s (antisymmetric ν_3 O=U=O), 668m, 642m, 634w, 616w (νU–O)
VII	3427m	3180br	1677m, 1638s, 1630m	1572s, 1508s	1458m	1364m	962s	464m, 434m	359m, 344m	3534br (coordinated water), 3326br (lattice water), 1514s, 1414s, 1388m, 1256s and 812m (bidentate chelating NO$_3^-$ group), 1373s, 828w (ionic nitrate), 664m, 645m, 630w, 614w (νTh–O)

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

TABLE III Physico-chemical measurements of the complex ligand $[ReO(H_4L)Cl]Cl_2$ and its heteronuclear complexes

Compound	*Molar conductance*[a] ($Ohm^{-1}\,cm^2\,mol^{-1}$)	$\mu_{complex}$[b] (B.M.)	λ_{max}[a] (nm)/(ε_{max} $L\,cm^{-1}\,mol^{-1}$)	δCOOH[c]	δNH	δH_2O Coordinated	δH_2O Lattice
$[ReO(H_4L)Cl]Cl_2$	94	0.07	288, 337, 362, 423 (2570), (1180), (1374), (327)	14.22 (2H)	8.45 (2H)	–	–
I	86	1.88	289, 337.5, 363, 437, 607 (2640), (880), (1205), (358), (416)	*	*	*	*
II	23	1.94	288, 337, 371, 429, 602 (2490), (965), (1345), (365), (404)	*	*	*	*
III	18	2.54	287, 339, 384, 439, 603 (2316), (924), (1417), (396), (377)	*	*	*	*
IV	108	0.08	288, 336.5, 374, 439, 544 (2162), (662), (1165), (334), (224)	14.34 (1H)	8.48 (2H)	3.35 (4H)	–
V	114	5.53	288, 337, 362, 480, 502, 711 (2385), (976), (1415), (448), (314), (168)	*	*	*	*
VI	57	0.06	287, 336.5, 366, 419, 514 (2471), (805), (1210), (387), (615)	14.28 (1H)	8.46 (2H)	3.30 (2H)	–
VII	62	0.05	285, 335.5, 365, 340, 522 (1557), (594), (1170), (352), (718)	14.30 (1H)	8.50 (2H)	3.50 (2H)	2.85 (2H)

[a] DMF Solutions, 1×10^{-3} M, at 28°C.

[b] Measurements were performed at 26°C, the magnetic moment included all cations in the complex.

[c] Chemical shifts with reference to TMS

*Measurement not made. Compound is paramagnetic.

TABLE IV Thermal analysis of heteronuclear complexes

Compound	*Temperature range* (°C)	*Loss in weight actual* (*calcd.*) (%)	*DSC peak* (°C)		ΔH (J g^{-1})	*Composition of residue*	*Probable composition of expelled groups*
			Endo	*Exo*			
I	40–102	1.25 (1.10)	84	–	40.27	$\{[ReO(H_3L)Cl]_2CuCl_2(OH_2)_2\}SO_4$	One molecule of lattice water
	102–170	3.22 (3.31)	163	–	14.18	$\{[ReO(H_3L)Cl]_2CuCl_2\}SO_4$	Two molecules of coordinated water
	170–276	13.87 (13.79)	273	–	7.90	$\{[ReO(HL)Cl]_2Cu\}$	Two molecules of HCl and one molecule of H_2SO_4[a]
	276–334	23.80 (23.67)	332	–	33.36	$\{[ReO(C_{21}H_{17}O_4N_4)]_2Cu$	Two molecules of HCl and two molecules of CO_2
II	50–180	4.10 (3.98)	177	–	16.00	$[ReO(H_3L)Cl_2Cu(SO_4)]$	Two molecules of coordinated water
	180–309	12.0 (12.04)	307	–	635.80	$[ReO(HL)Cu(SO_4)]$	Two molecules of HCl
III	50–193	6.83 (6.77)	177	–	10.62	$\{ReO(H_2L)Cl[Cu(OH_2)SO_4]_2\}$	Four molecules of coordinated water
	193–384	13.67 (13.58)	350	–	32.71	$\{ReO(HL)[CuSO_4]_2\}$	Two molecules of coordinated water and one molecule of HCl
IV	50–249	25.34 (25.12)	–	228	−152.15	$[ReO(HL)Ni]$	Two molecules of coordinated water, two molecules of HCl and two molecules of NO_3[b]
	249–328	34.90 (34.61)	326	–	55.14	$[ReO(C_{20}H_{17}O_2N_4)Ni]$	Two molecules of CO_2
V	50–225	12.95 (12.88)	–	223	–222.02	$[ReO(HL)Cl_3Fe(OH_2)_3]$	Two molecules of HNO_3
	225–334	37.05 (36.76)	–	330	–145.42	$[ReO(C_{20}H_{17}O_2N_4)FeO]$	Two molecules of coordinated water, three molecules of HCl and two molecules of CO_2
VI	50–253	13.85 (13.65)	–	229	–71.39	$[ReO(HL)UO_2(NO_3)]$	One molecule of coordinated water, two molecules of HCl and one molecule of NO_3[b]
	253–511	27.00 (27.04)	511	–	185.39	$[ReO(C_{20}H_{17}O_2N_4)UO_2]$	Two molecules of CO_2 and one molecule of NO_3[b]
VII	40–85	2.95 (2.96)	74	–	95.51	$[ReO(H_3L)Cl_3Th(NO_3)_2(OH_2)]NO_3$	Two molecules of lattice water
	85–168	4.50 (4.44)	147	–	14.10	$[ReO(H_3L)Cl_3Th(NO_3)_2]NO_3$	One molecule of coordinated water
	168–284	10.60 (10.44)	265	–	37.71	$[ReO(HL)ClTh(NO_3)_2]NO_3$	Two molecules of HCl
	184–527	36.20 (35.97)	459	–	12.73	$[ReO(C_{20}H_{17}O_2N_4)Th]$	One molecule of HCl, two molecules of CO_2 and three molecules of NO_3[b]

[a] H_2SO_4 may be eliminated as $SO_3(g) + H_2O(g)$.
[b] The NO_3 group may be eliminated as $NO_2(g) + ½O_2(g)$.

Conductivity Measurements

Conductivity measurements, Table III, indicate that complexes **I**, **IV**, **V**, **VI** and **VII** are 1 : 1, 1 : 2, 1 : 2, 1 : 1 and 1 : 1 electrolytes, respectively, while complexes **II** and **III** are non-electrolytes. The colors of solutions of the dissolved complexes did not change during or after measurements. The lower values of the molar conductance of complexes **II** and **III** indicate that either Cl^- or H_2O in the *trans* positions was not replaced by DMF.

The sulfate ion in complex **I** was detected by adding a solution of $BaCl_2$ and the chloride ion in complex **VI** was detected by adding a solution of $AgNO_3$, confirming the electrolytic nature of these complexes. The relatively low values of the measured conductivity may be due to the bulky cations which contain the Re=O(V) ion and heterometal ion(s).

Electronic Spectra and Magnetic Moments of the Complexes

The magnetic measurement data and the values of λ_{max} and molar absorptivities (ε), are presented in Table III.

Comparison of electronic spectra of the complex ligand $[ReO(H_4L)Cl]Cl_2$ and its heteronuclear complexes showed the appearance of new bands in the range 502–711 nm, which may be assigned to either charge transfer or d → d transitions of the heterometal ions.

The magnetic moment values for heteronuclear complexes (**I**) and (**II**), which contain only one Cu(II) ion, are 1.88 and 1.94 B.M., respectively. These values are slightly higher than the spin value (1.73 B.M.) expected for one unpaired electron, indicating octahedral geometry around Cu(II) [34]. The magnetic moment value of the hetero-trinuclear complex (**III**), which contains two Cu(II) ions, is 2.54 B.M.

The electronic spectra of complexes **I**, **II** and **III** exhibit new bands at 607 nm ($\varepsilon = 416$), 602 nm ($\varepsilon = 404$) and 603 nm ($\varepsilon = 377$) respectively, assigned to the $^2E_g \rightarrow {}^2T_{2g}$ transition of octahedral geometry [35,36]. On the basis of the above discussion, an octahedral geometry may be assigned to the heteronuclear complexes of oxorhenium(V) and Cu(II) as shown in Fig. 2, structures **I**, **II** and **III**.

The visible spectrum of the diamagnetic heteronuclear Ni(II) complex (**IV**), showed a band at 544 nm ($\varepsilon = 224$), similar to that reported for square-planar geometry [37].

The electronic spectra of Fe(III) chelates showed two new bands at 502 nm ($\varepsilon = 314$) and 711 nm ($\varepsilon = 168$), which are assigned to the $^6A_1 \rightarrow {}^4A_1$, $^4E(G)$ and $^6A_1 \rightarrow {}^4T_2$ (G) transitions. These spectral data as well as the magnetic moment value of 5.53 B.M. are comparable with those reported for octahedral Fe(III) ion [38,39]. The proposed structures of complexes **IV** and **V** are shown in Fig. 3.

Electronic spectra of the diamagnetic heteronuclear complexes of UO_2(VI) and Th(IV), **VI** and **VII** exhibit absorption bands at 514 and 522 nm, respectively, attributed to charge transfer from the complex ligand to the heterocations. The suggested structures of the heteronuclear complexes of UO_2(VI) and Th(IV) are eight-coordinate complexes, i.e., distorted dodecahedral geometry, Fig. 4. The IR spectrum of the unusual eight-coordinate UO_2(VI) complex shows a strong absorption band at 912 cm^{-1} assigned to the antisymmetric ν_3(O=U=O) vibration [40].

Nuclear Magnetic Resonance Spectral Studies

The assignments of the main signals in the ^1H NMR spectra of the complex ligand $[ReO(H_4L)Cl]Cl_2$, and its diamagnetic heterometal complexes are listed in Table III. In complexes **IV**, **VI** and **VII**, the signal due to the amide protons appears at δ 8.46–8.50 ppm (2H), similar to that of the complex ligand which appears at δ 8.45 ppm (2H).

The signal corresponding to the carboxylic groups appears at δ 14.22 ppm (2H) in the complex ligand. In its complexes **IV**, **VI** and **VII** the signal appears in the same range, δ 14.28–14.34 ppm (1H). The integration of protons of the carboxylic groups in the diamagnetic heterometal complexes indicates deprotonation of only one carboxylic group.

Complexes **IV**, **VI** and **VII** showed the signal corresponding to the coordinated water molecules at δ 3.35 ppm (4H), 3.30 ppm (2H) and 3.50 ppm (2H), respectively, while the signal due to the lattice water molecules in complex **VII** was observed at δ 2.85 ppm (4H) [41]. The existence of lattice and coordinated water molecules in the complexes was further confirmed by thermal analyses.

Mass Spectra

The mass spectra of the heteronuclear complexes **II**, **IV** and **V** as representative examples provide good evidence for the molecular formulas of these complexes. Mass spectral data are consistent with the formulation $[ReO(H_3L)Cl_2CuSO_4]$ (**II**), $[ReO(H_3L)Cl_2Ni](NO_3)_2$ (**IV**) and $[ReO(H_3L)Cl_3Fe](NO_3)_2$ (**V**), which give the parent ions at m/z 868.73 u (calculated value 868.16 u after subtraction of two coordinated water molecules), 892.05 u (calculated value 891.25 u after subtracting two coordinated water molecules) and 924.36 u (calculated value 923.88 u after subtracting three coordinated water molecules), respectively.

Thermal Analyses

The results of TG-DSC analyses of the heteronuclear complexes are shown in Table IV. The loss of water of crystallization from complexes **I** and **VII** occurs in the temperature range 40–102°C. Elimination of lattice water was accompanied by an endothermic peak with $\Delta H=40.27$ and $95.51\ J\,g^{-1}$, respectively.

The coordinated water molecules were eliminated in one step for complexes **I**, **II** and **VII** at 170, 180 and 168°C, respectively. Elimination of coordinated water from complex **I**, gives the isolable complex $\{[ReO(H_3L)Cl]_2CuCl_2\}SO_4$. Elimination of coordinated water molecules was accompanied by the loss of NO_3 groups and/or HCl molecules in complexes **III**, **IV** and **VI**, while complex **V** loses two HNO_3 molecules at 223°C with $\Delta H = -222.02\ J\,g^{-1}$ to give the isolable complex $[ReO(HL)Cl_3Fe(OH_2)_3]$. This exothermic process may be due to elimination of the protons of the NH groups of the tetraaza ring which neutralize the nitrate anions.

All complexes lose HCl molecules from the chloride ions and the protons of the NH groups of the tetraaza ligand; in a similar way complex **I** also loses H_2SO_4 and complex **V** loses HNO_3. Elimination of CO_2 molecules occurs at temperatures $> 320°C$, through decarboxylation.

Pyrolytic Preparation and Characterization of Heteronuclear Complexes

New solid heteronuclear complexes were prepared pyrolytically from the mother complexes **I** and **V**. A certain amount of the original complex was placed in a porcelain crucible and heated in an oven to a fixed temperature, on the basis of the results of thermal analyses. The material was heated for 30 min, then placed in a desiccator to cool to room temperature and weighed. The previous steps were repeated until it reached a constant weight. Structures of the obtained products are discussed on the basis of their IR and UV-visible spectra, magnetic moments, conductivity measurements and elemental analyses for rhenium, copper, iron and chlorine.

$\{[ReO(H_3L)Cl]_2CuCl_2\}SO_4$ (**VIII**) was prepared by heating complex **I** to 163°C to constant weight. The color of the complex changed from olive-green to greenish-violet.

$$\underset{\textbf{I}}{\{[ReO(H_3L)Cl]_2CuCl_2(OH_2)_2\}SO_4 \cdot H_2O} \xrightarrow{163^\circ C} \underset{\textbf{VIII}}{\{[ReO(H_3L)Cl]_2CuCl_2\}SO_4} + 3H_2O$$

Its IR spectrum is similar to complex **I**, except for the disappearance of bands at 3530 and 3315 cm^{-1}, due to coordinated and lattice water molecules, respectively. Conductivity measurements on the thermal product in DMF solution showed the presence of ionic sulfate ($\Lambda_M = 92\,\mathrm{Ohm^{-1}\,cm^2\,mol^{-1}}$).

The measured magnetic moment was 1.79 B.M., which with the band at 638 cm^{-1} assigned to a $^2B_{1g} \rightarrow {}^2A_{1g}$ transition, supports the square planar geometry around Cu(II).

From the previous results and the elemental analyses for rhenium, copper and chlorine, the product obtained on heating can be represented as $\{[ReO(H_3L)Cl]_2CuCl_2\}SO_4$ (**VIII**) and its proposed structure is shown in Fig. 5.

$[ReO(HL)Cl_3Fe(OH_2)_3]$ (**IX**) was also prepared by heating complex **V** at 223°C to constant weight. The color of the product was deep brown.

$$\underset{\textbf{V}}{[ReO(H_3L)Cl_3Fe(OH_2)_3](NO_3)_2} \xrightarrow{223^\circ C} \underset{\textbf{IX}}{[ReO(HL)Cl_3Fe(OH_2)_3]} + 2HNO_3$$

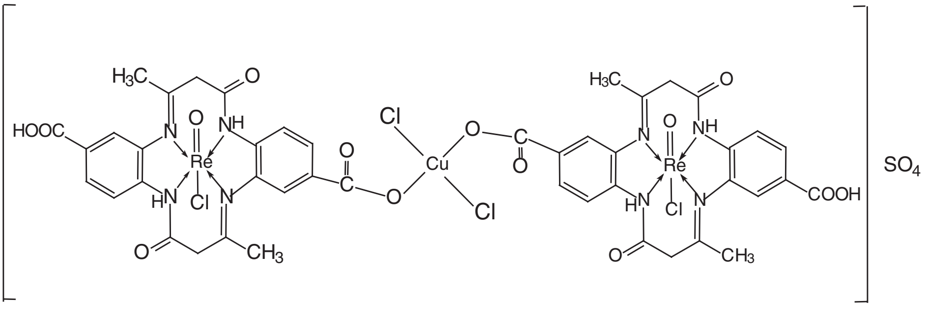


FIGURE 5 Structure of $\{[ReO(H_3L)Cl]_2CuCl_2\}SO_4$ (**VIII**), dichlorocopper(II) bis[chloro(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[*a*,*h*][14]annulene-2,11-dicarboxylic acid) oxorhenium(V)] sulphate complex, obtained by heating complex **I** to 163°C.

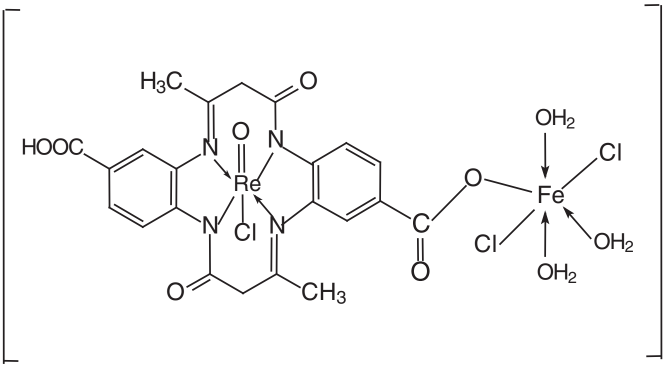


FIGURE 6 Structure of [ReO(HL)$Cl_3Fe(OH_2)_3$] (**IX**), triaquadichloroiron(III) [chloro(8,17-dimethyl-6,15-dioxo-5,7,14,16-tetrahydrodibenzo[*a*,*h*][14]annulene-2,11-dicarboxylic acid) oxorhenium(V)] complex, obtained by heating complex **V** to 223°C.

The IR spectrum showed the disappearance of bands at 3190, 1380 and 828 cm^{-1} due to νNH and the nitrate ions, respectively. Conductivity measurements in DMF solution showed that the heated product is a non-electrolyte, which confirms the elimination of the nitrate ions.

The magnetic moment of the heated product was 5.62 B.M. Its electronic spectrum showed visible bands at 506 nm ($\varepsilon = 327$) and 709 nm ($\varepsilon = 159$), which are assigned to $^6A_1 \rightarrow {}^4A_1$, $^4E(G)$ and $^6A_1 \rightarrow {}^4T_2(G)$ transitions, indicating that the heterometal Fe(III) has octahedral geometry [38,39].

From the previous results and the elemental analyses of rhenium, iron and chlorine, the heated product can be represented as [ReO(HL)$Cl_3Fe(OH_2)_3$] (**IX**) and its proposed structure is shown in Fig. 6.

Antibacterial Activities

The complex ligand [ReO(H_4L)Cl]Cl_2 and its heterometal complexes were tested against the bacterial species *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas aeruginosa* and *Escherichia coli*. Some antibiotics were also evaluated for their antibacterial activities and their results are compared with the complex ligand and its heterometal complexes. The results are tabulated in Tables V and VI.

The heteronuclear complexes **I**–**IX** showed enhanced activity toward *S. aureus*, *B. subtilis* and *P. aeruginosa* compared with the complex ligand. Heteronuclear complex **IV** had the same activity towards *S. aureus* as the complex ligand, and complexes **IV**, **VI** and **VII** had the same activity toward *B. subtilis* as the complex ligand. Complexes **IV**, **VI**, **VII**, **VIII** and **IX** had the same activity towards *P. aeruginosa* as the complex ligand.

The complex ligand [ReO(H_4L)Cl]Cl_2 shows higher antibacterial activity towards *E. coli* than that its heterometal complexes.

Comparison of the biological activities of the complex ligand and its heterometal complexes and some known antibiotics shows the following results:

(1). The heterometallic complexes show higher antibacterial effects towards *S. aureus*, *B. subtilis* and *P. aeruginosa* than Amikacin, Septrin, Cefobid, Ampicillin and Traivid.

TABLE V Antibacterial activity of the complex ligand $[ReO(H_4L)Cl]Cl_2$ and its heteronuclear complexes

Compound	*Gram +ve* *Staphylococcus aureus*	*Gram −ve*		
		Bacillus subtilis	*Pseudomonas aeruginosa*	*Escherichia coli*
$[ReO(H_4L)Cl]Cl_2$	++	++	++	+++
I	+++	+++	+++	++
II	+++	+++	+++	++
III	+++	+++	+++	+
IV	++	++	++	+
V	+++	+++	+++	++
VI	+++	++	++	+
VII	+++	++	++	+
VIII	+++	+++	++	++
IX	+++	+++	++	++

The test was done using the diffusion agar technique.
Well diameter: 0.6 cm.
Inhibition values = 0.1–0.5 cm beyond control = + (less active).
Inhibition values = 0.6–1.0 cm beyond control = ++ (moderate active).
Inhibition values = 1.1–1.5 cm beyond control = +++ (highly active).

TABLE VI Antibacterial activity of some antibiotics

Antibiotic	*Cocci* (*gram +ve*) *Staphylococcus aureus*	*Bacilli* (*gram–ve*)		
		Pseudomonas aeruginosa	*Klebsiella*	*Escherichia coli*
Amikacin	++	+++	+++	++
Doxycllin	+++	++	+++	++
Augnantin	+++	++	+++	+++
Sulperazon	+++	+++	+++	++
Unasyn	+++	++	++	++
Septrin	++	++	++	++
Cefobid	++	++	++	++
Ampicillin	++	++	++	++
Nitrofurantion	+++	++	+++	++
Traivid	++	++	+++	+++
Erythromycin	+++	++	++	++

The test was done using the diffusion agar technique.
Well diameter: 0.6 cm.
Inhibition values = 0.1–0.5 cm beyond control = + (less active).
Inhibition values = 0.6–1.0 cm beyond control = ++ (moderate active).
Inhibition values = 1.1–1.5 cm beyond control = +++ (highly active).

(2). The complex ligand and other heterometallic complexes show antibacterial effects equal to those of some antibiotics.

From all of the above results, we conclude that the complex ligand $[ReO(H_4L)Cl]Cl_2$ and its heterometallic complexes show antibacterial effects similar to those of the investigated antibiotics and greater effects in some cases.

References

[1] M.B. Shaddan, F.R. Wüst and J.A. Katzenellenbogen, *J. Org. Chem.* **64**, 8108 (1999).
[2] F. Wüst, M.B. Shaddan, P. Leibnitz, H. Spies, J.A. Katzenellenbogen and B. Johannsen, *Bioorg. Med. Chem.* **7**, 1827 (1999).
[3] P. Kofod, P. Moore and N.W. Alcock, *Acta Chem. Scand.* **47**, 1083 (1993).
[4] J. Eilmes, *Polyhedron* **11**, 581 (1992).

[5] J.C. Dabrowiak, D.P. Fisher, F.C. McElory and D.J. Macero, *Inorg. Chem.* **18**, 2304 (1979).
[6] C.L. Bailey, R.D. Bereman and D.P. Rillema, *Inorg. Chem.* **25**, 3149 (1986).
[7] B. Keita, Y.W. Lu and J. Napjo, *J. Electroanal. Chem.* **367**, 285 (1994).
[8] A. Deronzier and M.J. Marques, *J. Electroanal. Chem.* **370**, 151 (1994).
[9] P. Stavropoulos, P.G. Edwards, G. Wilkinson, M. Motevalli, K.M. Abdul Malik and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.* 2167 (1985).
[10] M.P. Egloff, P.T. Cohen, P. Reinermer and D. Barford, *J. Mol. Biol.* **254**, 942 (1995).
[11] D.E. Fenton and A.G. Sykes, Advances in Inorganic and Bioinorganic Mechanisms (Academic Press, London, 1983), Vol. 2, p. 187.
[12] L.F. Lindoy, *Pure Appl. Chem.* **61**, 1575 (1989).
[13] C.J. Burrows, J.G. Muller, G.T. Poulter and S.E. Rokita, *Acta. Chem. Scand.* **50**, 337 (1996).
[14] M.G. Bhowon, H.L. Wah and R. Naram, *Polyhedron* **18**, 341 (1999).
[15] E.J. Larson and V.L. Pecoraro, *J. Am. Chem. Soc.* **113**, 3810 (1991).
[16] C.A. Solata, M.T. Youinou and C.J. Burrows, *Inorg. Chem.* **30**(18), 3454 (1991).
[17] M.M. Mashaly, *J. Coord. Chem.* **56**(10), 833 (2003).
[18] B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.* 331 (1959).
[19] W. Geilmann and A. Voigt (1930). *Z. Anorg. Allgen. Chem.* **193**, 311.
[20] Z.H. Chohan and S.K.A. Sherazi, *Synth. React. Inorg. Met.-Org. Chem.* **29**(1), 105 (1999).
[21] C. Jayobalakrishnan and K. Natarajan, *Synth. React. Inorg. Met.-Org. Chem.* **31**(6), 983 (2001).
[22] T. Jeewoth, H.L.K. Wah, M.G. Bhowon, D. Ghoorhoo and K. Babooram, *Synth. React. Inorg. Met.-Org. Chem.* **30**(6), 1023 (2000).
[23] M.B. Ferrari, S. Capacchi, G. Pelosi, G. Reffo, P. Tarasconi, R. Albertini, S. Pinelli and P. Lunghi, *Inorg. Chem. Acta* **286**, 134 (1999).
[24] N. Dharmaraj, P. Viswanathamurthi and K. Natarajan, *Transition Met. Chem.* **26**, 105 (2001).
[25] K. Nakamoto, Infrared Spectra of Inorganic and Coordinated Compounds (John Wiley & Sons, New York, 1977), 3rd Edn.
[26] M.M. Mashaly, *Synth. React. Inorg. Met.-Org. Chem.* **26**, 211 (1996).
[27] M.M. Mashaly and M. El-Behairy, *Polish J. Chem.* **71**, 705 (1997).
[28] M.M. Mashaly, *J. Coord. Chem.*, **48**, 165 (1999).
[29] A.A. Amindjanov and N.M. Korbanov, *Kompleksoobraz. V. Rastvorakh Tadzh Gos. Un-t, Dushanbe* (USSR) **1**, 118 (1991); *Chem. Abstr.* **120**, 825 (1994).
[30] J. Chaff and G.A. Rower, *Chem. Ind.* 92 (1962).
[31] C. Bolzati, F. Tisato, F. Refosco, G. Bandoli and A. Dolmella, *Inorg. Chem.* **35**, 6221 (1996).
[32] E. Shuter, H.R. Hoveyda, V. Karunaratne, S.J. Rettig and C. Orvig, *Inorg. Chem.* **35**, 368 (1996).
[33] Z.M. Miodragovic, G. Vuckovic, V.M. Leove and V.M. Buzash, *Synth. React. Inorg. Met.-Org. Chem.* **30**(1), 57 (2000).
[34] B.K. Patel and M.M. Patel, *J. Ind. Chem. Soc.* **67**, 186 (1990).
[35] L. Sacconi, M. Champdini and U. Campigli, *Inorg. Chem.* **4**, 407 (1965).
[36] N.H. Patel, K.M. Patel, K.N. Patel and M.N. Patel, *Synth. React. Inorg. Met.-Org. Chem.* **31**(6), 1031 (2001).
[37] R.H. Holm, *J. Am. Chem. Soc.* **82**, 5632 (1960).
[38] J.C. Bailar, H.J. Emeleus, J.R. Nyholm and A.F. Dickenson, Comprehensive Inorganic Chemistry (Pergamon Press, Oxford, 1975), Vol. 3, p. 517.
[39] R.C. Saxena, C.L. Jain, S. Rastogi and J.L. Vats, *Inorg. Chim. Acta* **16**, 103 (1976).
[40] V.V. Savant and C.C. Patel, *J. Inorg. Nucl. Chem.* **31**, 2319 (1969).
[41] J.M. Ouyang, W.H. Lin, Z.M. Zhang and C.Y. Jiang, *Synth. React. Inorg. Met.-Org. Chem.* **30**(1), 1 (2000).