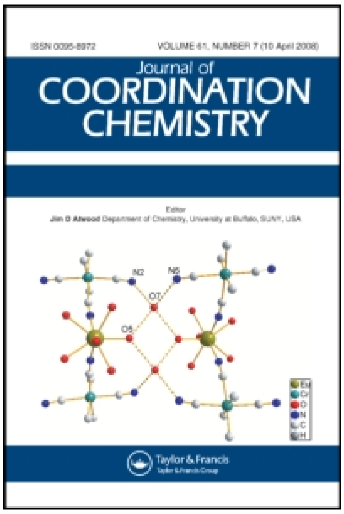

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Heteronuclear complexes of oxorhenium(V) with Fe(III), Co(II), Ni(II), Cu(II), Cd(II) and UO_2(VI) and their biological activities

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HETERONUCLEAR COMPLEXES OF OXORHENIUM(V) WITH Fe(III), Co(II), Ni(II), Cu(II), Cd(II) AND UO_2(VI) AND THEIR BIOLOGICAL ACTIVITIES

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Heteronuclear complexes containing oxorhenium(V), with Fe(III), Co(II), Ni(II), Cu(II), Cd(II) and UO_2(VI) ions were prepared by the reaction of the complex ligands $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$ (**a**) and/or $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$ (**b**), where 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), with transition and actinide salts. Heterodinuclear complexes of ReO(V) with Fe(III), Co(II), Ni(II), Cu(II) and Cd(II) were obtained using a 1 : 1 mole ratio of the complex ligand and the metal salt. Heterotrinuclear complexes were obtained containing ReO(V) with UO_2(VI) and Cu(II) using 2 : 1 mole ratios of the complex ligand and the metal salts. The complex ligands **a** and **b** coordinate with the heterometal ion via a nitrogen of the heterocyclic ring and the nitrogen atom of the $C{=}N^7$ group. All transition metal cations in the heteronuclear complexes have octahedral configurations, while UO_2(VI) complexes have distorted dodecahedral geometry. The structures of the complexes were elucidated by IR, ESR, electronic and ^1H NMR spectra, magnetic moments, conductance and TG-DSC measurements. The antifungal activities of the complex ligands and their heteronuclear complexes towards *Alternaria alternata* and *Aspergillus niger* showed comparable behavior with some well-known antibiotics.

Keywords: Antifungal activity; Oxorhenium; Heteronuclear; Metal complexes

INTRODUCTION

Interest in using ^{186}Re and ^{188}Re radioisotopes in therapeutic nuclear medicine [1] led to the preparation of stable rhenium coordination complexes [2]. The ligand, *N*-isonicotinoyl-*N′*-thiobenzoylhydrazine (HINTB), shows fungitoxic activity of 27–48%, whereas its metal complexes show 30–98% fungitoxicity at concentrations of 750 and 1000 ppm. $[Zn(HINTB)_2Cl_2]$ and $[Zn(INTB)_2]$ show greater fungitoxicity than $[Cu(HINTB)Cl_2]$, $[Ni(HINTB)_2Cl_2]$, $[Co(HINTB)_2Cl_2]$, $[Cu(INTB)(CH_3COO)]$ and the ligand, as expected from the more basic nature of Zn(II) compared to other metal ions [3].

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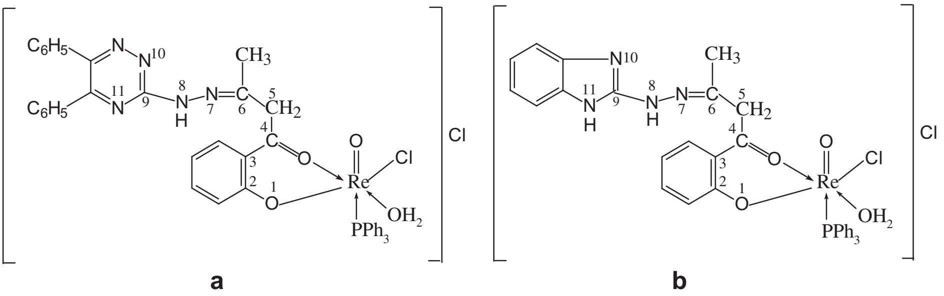


FIGURE 1 Structures of the complex ligands. **a** Aquachlorotriphenylphosphine-1-(2-hydroxyphenyl) butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone) oxorhenium(V) chloride complex. **b** Aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone) oxorhenium(V) chloride complex.

Schiff bases and their transition metal complexes exhibit biological activity as antibiotics, antivirus and antitumor agents because of their specific structures [4,5]. The *in vitro* antimicrobial activity of transition metal complexes and their organic ligands was tested against microorganisms such as *Salmonella typhi, Staphylococcus aureus, Klebsiella pneumeniae, Pseudomones aeruginose* and *Aspergillus niger* [6]. Most metal chelates have higher antimicrobial activity than free ligands.

Hydrazone complexes of Co(II), Ni(II) and Cu(II) have been used as antimalarial [7] and antidiabetic [8] agents, as well as in treatment of diseases such as leprosy and tuberculosis [9].

Mixed metal complexes constitute an important part of modern inorganic chemistry as active sites in a variety of metalloenzymes [10,11] and a significant and expanding role in industrial [11] and materials chemistry [13–16].

Herein, we report the synthesis and characterization of heteronuclear complexes using the complex ligands $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$ and $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$, (Fig. I) as N-N-donor ligands and their coordinating behavior toward Fe(III), Co(II), Ni(II), Cu(II), Cd(II) and UO_2(VI) ions.

EXPERIMENTAL

The complex ligands $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$ (**a**) and $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$ (**b**) (Fig. 1), were prepared by a literature method [17]. $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 2\frac{1}{2}H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ and $UO_2(NO_3)_2 \cdot 6H_2O$ were obtained from BDH, Analar or Merck. Ethanol, methanol, 1,4-dioxane, acetone, DMF, diethyl ether and DMSO were reagent grade.

Preparation of the Heteronuclear Complexes

$[ReO(L^1)(PPh_3)(OH_2)ClFe(NO_3)(OH_2)Cl]NO_3 \cdot H_2O$ (1) and $[ReO(HL^2)(PPh_3)(OH_2)ClFe(NO_3)(OH_2)Cl]NO_3 \cdot H_2O$ (8)

An ethanolic solution ($30\,cm^3$) containing 0.35 g (0.87 mmol) of $Fe(NO_3)_3 \cdot 9H_2O$ was added to an ethanolic solution ($50\,cm^3$) containing 0.85 g (0.87 mmol) of the complex ligand $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$ or 0.75 g (0.87 mmol) of the complex ligand $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$. The solutions were refluxed for 2 h and allowed to cool to room temperature when the formed precipitates were filtered, washed several times with a mixture of 50% (v/v) ethanol–water then with diethyl ether, and finally air-dried. The products isolated were 0.72 g (69%), chocolate-brown, and 0.61 g (65%), brown, solids, respectively.

$[ReO(L^1)(PPh_3)(OH_2)ClCo(NO_3)(OH_2)Cl]\cdot H_2O$ (2) and $[ReO(HL^2)(PPh_3)(OH_2)ClCo(NO_3)(OH_2)Cl]\cdot H_2O$ (9)

An ethanolic solution (30 cm^3) containing 0.25 g, (0.87 mmol) of $Co(NO_3)_2\cdot 6H_2O$ was added to an ethanolic solution (50 cm^3) containing 0.85 g, (0.87 mmol of the complex ligand $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$ or 0.75 g, (0.87 mmol) of the complex ligand $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$. The solutions were refluxed for 3 h. After cooling to room temperature, the formed precipitates were filtered, washed with a mixture of 50% (v/v) ethanol–water then with diethyl ether, and finally air-dried. The products isolated were 0.73 g (74%), dark green, and 0.59 g (66%), green, solids, respectively.

$[ReO(L^1)(PPh_3)(OH_2)ClNi(NO_3)(OH_2)Cl]\cdot H_2O$ (3) and $[ReO(HL^2)(PPh_3)(OH_2)ClNi(NO_3)(OH_2)Cl]\cdot H_2O$ (10)

These complexes were prepared in a similar way to Complexes **2** and **9** except that $Ni(NO_3)_2\cdot 6H_2O$ was used instead of $Co(NO_3)_2\cdot 6H_2O$. The products obtained were 0.69 g (70%), green, and 0.60 g (67%), light green, solids, respectively.

$[ReO(L^1)(PPh_3)(OH_2)ClCu(NO_3)(OH_2)Cl]\cdot H_2O$ (4) and $[ReO(HL^2)(PPh_3)(OH_2)ClCu(NO_3)(OH_2)Cl]\cdot H_2O$ (11)

An ethanolic solution (30 cm^3) containing 0.20 g, (0.87 mmol) of $Cu(NO_3)_2\cdot 2\frac{1}{2}H_2O$ was added to an ethanolic solution (50 cm^3) containing 0.85 g (0.87 mmol) of the complex ligand $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$ or 0.75 g (0.87 mmol) of the complex ligand $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$. The solutions were refluxed for 3 h. After cooling to room temperature, the formed precipitates were filtered, washed with a mixture of 50% (v/v) ethanol–water, then with diethyl ether, and finally air-dried to give 0.72 g (73%), grayish-green, and 0.62 g (70%), green, solids, respectively.

$\{[ReO(L^1)(PPh_3)(OH_2)Cl]_2CuCl_2\}\cdot H_2O$ (5) and $\{[ReO(HL^2)(PPh_3)(OH_2)Cl]_2CuCl_2\}\cdot H_2O$ (12)

These complexes were prepared in a similar way to Complexes **4** and **11** except that the amount of $Cu(NO_3)_2\cdot 2\frac{1}{2}H_2O$ was reduced to half (0.10 g, 0.44 mmol) and the time of heating was 5 h. The products isolated were 0.68 g (76%), brown, and 0.56 g (71%), green, solids, respectively.

$[ReO(L^1)(PPh_3)(OH_2)ClCd(NO_3)(OH_2)Cl]$ (6) and $[ReO(HL^2)(PPh_3)(OH_2)ClCd(NO_3)(OH_2)Cl]$ (13)

An ethanolic solution (30 cm^3) containing 0.27 g (0.87 mmol) of $Cd(NO_3)_2\cdot 4H_2O$ was added to an ethanolic solution (50 cm^3) containing 0.85 g (0.87mmol) of the complex ligand $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$ or 0.75 g, (0.87 mmol) of the complex ligand

$[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$. The solutions were refluxed for 4 h. The solutions were allowed to cool to room temperature. The solid products were obtained by filtration, washed with a mixture of 50% (v/v) ethanol–water, then diethyl ether and finally air-dried. The products obtained were 0.73 g (72%), brown, and 0.66 g (72%), gray, solids, respectively.

$\{[ReO(L^1)(PPh_3)(OH_2)Cl]_2UO_2(OH_2)_2\}Cl_2$ (7) and $\{[ReO(HL^2)(PPh_3)(OH_2)Cl]_2UO_2(OH_2)_2\}Cl_2$ (14)

An ethanolic solution (30 cm^3) containing 0.44 g, (0.87 mmol) of $UO_2(NO_3)_2 \cdot 6H_2O$ was added to an ethanolic solution (50 cm^3) containing 1.70 g (1.74 mmol) of the complex ligand $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$ or 1.50 g (1.74 mmol) of the complex ligand $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$. The solutions were refluxed for 4 h. After cooling to room temperature, the formed precipitates were filtered, washed several times with a mixture of 50% (v/v) ethanol–water then with diethyl ether, and finally air-dried. The products obtained were 1.37 g (70%), reddish brown, and 1.26 g (72%), lemon green, solids, respectively.

All the heteronuclear complexes are soluble in DMF and DMSO and partially soluble in ethanol. Complexes **6**, **7**, **13** and **14** are partially soluble in 1,4-dioxane while the other complexes are insoluble.

Antifungal Studies

Screening antifungal studies for the compounds were performed using the disc diffusion method [18,19] 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 and then divided by the number of moles of each complex.

Physical Measurements and Analyses

^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. 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 [20]. 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. Electronic spectra of solutions of the complexes in DMF were recorded on a Jasco model V-550 UV–Vis spectrophotometer. Infrared 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. ESR spectra of the copper(II) complexes were recorded for polycrystalline samples at room temperature on a JEOL microwave unit, JES-FE_2XG spectrometer at the Central Laboratories, Tanta University, Tanta, Egypt. The magnetic field was calibrated with a 2,2-diphenyl-1-picrylhydrazyl sample purchased from Aldrich. Microanalyses of carbon, hydrogen, nitrogen and phosphorus were carried out at the Microanalytical Center, Cairo University, Giza, Egypt. Analyses of metals were carried out on an Optima 3000 Perkin-Elmer inductively coupled plasma instrument (ICP). Chloride ion was determined gravimetrically as silver chloride [21]. Conductivities were measured on solutions of the complexes in DMF (1×10^{-3}M) using a Wissenschaftlich–Technische Werkstatten, D 8120 Weilheim, Germany, Model LBR 40A, conductivity meter.

RESULTS AND DISCUSSION

Reaction of the complex ligand $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$ (**a**) and/or $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$ (**b**) with the metal salts $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 2\frac{1}{2}H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$ in the mole ratio (1:1) yielded the heterobinuclear complexes, $[ReO(L^1 \text{ or } HL^2)(PPh_3)(OH_2)ClFe(NO_3)(OH_2)Cl]NO_3 \cdot H_2O$ (**1**) and (**8**), $[ReO(L^1 \text{ or } HL^2)(PPh_3)(OH_2)ClCo(NO_3)(OH_2)Cl] \cdot H_2O$ (**2**) and (**9**), $[ReO(L^1 \text{ or } HL^2)(PPh_3)(OH_2)ClNi(NO_3)(OH_2)Cl] \cdot H_2O$ (**3**) and (**10**), $[ReO(L^1 \text{ or } HL^2)(PPh_3)(OH_2)ClCu(NO_3)(OH_2)Cl] \cdot H_2O$ (**4**) and (**11**) and $[ReO(L^1 \text{ or } HL^2)(PPh_3)(OH_2)ClCd(NO_3)(OH_2)Cl]$ (**6**) and (**13**), Figs. 2–5. Reaction of complex ligands **a** or **b** with $UO_2(NO_3)_2 \cdot 6H_2O$ in the mole ratio (2:1) yielded the heterotrinuclear complexes $[ReO(L^1 \text{ or } HL^2)(PPh_3)(OH_2)Cl]_2UO_2(OH_2)_2\}Cl_2$ (**7**) and (**14**), Figs. 6 and 7. Heterotrinuclear complexes $\{[ReO(L^1 \text{ or } HL^2)(PPh_3)(OH_2)Cl]_2 CuCl_2\} \cdot H_2O$ (**5**) and (**12**) were also obtained by mixing the complex ligands **a** or **b** respectively with the Cu(II) ion in a 2:1 mole ratio, Figs. 8 and 9.

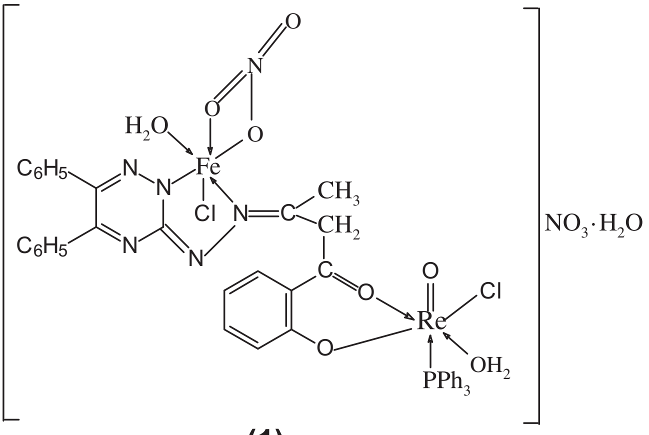
Addition of metal salts to the complex ligand $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$ (**a**) and/or $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$ (**b**) does not replace the oxorhenium(V) ion from its coordination sites (OO); the heterometal coordinates via one of the nitrogen atoms of the heterocyclic ring and the CN group. The isolated heteronuclear complexes were amorphous upon removal of the solvent. Tables I–IV show the results obtained from the analyses and physical investigations.

IR Spectra

The IR spectra of the complex ligands **a** and **b** and their heterometal complexes are listed in Table II. The IR spectrum of ligand **a** showed bands at 3128 (νNH^8), 1662 ($\nu C{=}O$), 1588 (νCN^7) and $1530\,cm^{-1}$ (νCN of the heterocyclic ring and νCN^8) while ligand **b** showed bands at 3159 (νNH^8), 3119 (νNH ring), 1651 ($\nu C{=}O$), 1580 (νCN^7) and $1516\,cm^{-1}$ (νCN of the heterocyclic ring and (νCN^8). The stretching frequencies of CO and CN (ring) and CN^8 in the ligands were unaffected in all heterometal complexes. Also, νNH (ring) in ligand **b** was not affected in its heterometal complexes, indicating that these groups are not involved in coordinating to the metal cations.

The stretching vibrations of νCN^7 were shifted to lower frequency by 26–46 and 22–38 in heteronuclear complexes of **a** and **b**, respectively, indicating the participation of this group in coordinating to the metal cations.

IR spectra of **a** and **b** lacked the band due to νNH^8. The disappearance of this proton was also confirmed by ^1H NMR (see below). This indicates the complex ligands are in the form of tautomer II, Figs. 10 and 11.



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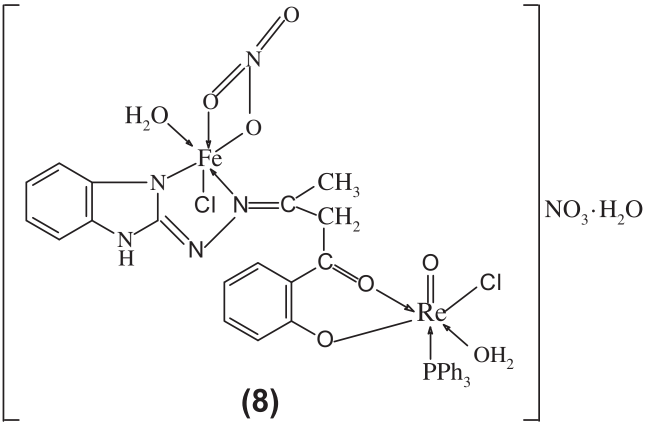

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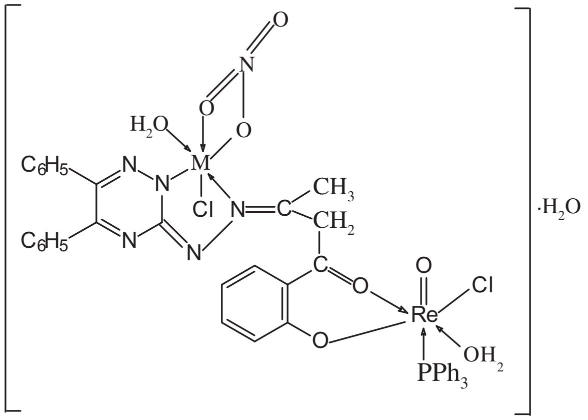
FIGURE 2 Structures of heteronuclear complexes of oxorhenium(V) and Fe(III) ion, obtained by using the mole ratio 1:1 of complex ligand **a** or **b** to ferric ion. (**1**)Aquachloronitratoiron(III)[aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone)oxorhenium(V)] nitrate monohydrate complex. (**8**) Aquachloronitratoiron(III)[aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione- 3-(1*H*-benzimidazol-2-ylhydrazone)oxorhenium(V)]nitrate monohydrate complex.

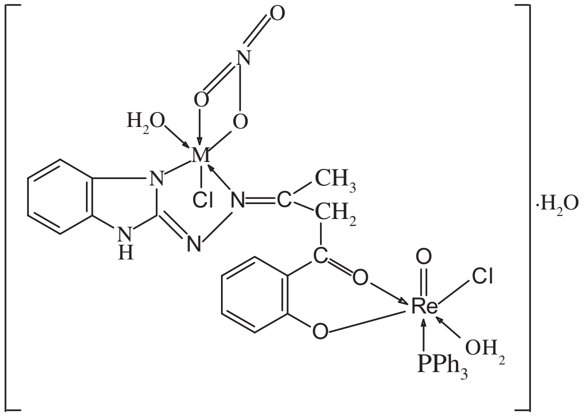
A band attributable to νReO for the mononuclear complex ligands **a** and **b** was observed at 997 cm^{-1} and for all heteronuclear complexes appeared in the range 996–1002 cm^{-1}, consistent with values previously reported for similar oxorhenium(V) complexes [22–30].

The stretching vibration of the coordinated water molecules appears at 3486–3509 cm^{-1} in the heteronuclear complexes. A new band at 3347–3383 cm^{-1} was observed in the spectra of the heteronuclear complexes, except for Complexes **6**, **7**, **13** and **14**, due to H-bonded lattice water molecules.

The stretching vibrations of the ionic nitrate group were observed as two bands in the ranges 1369–1373 cm^{-1} and 828–829 cm^{-1} for Complexes **1** and **8**. Heteronuclear complexes other than Complexes **5**, **7**, **12** and **14** showed bands due to the bidentate chelating nitrate group at 1436–1439, 1376–1388, 1201–1227 and 805–830 cm^{-1}, similar to those previously reported for coordinated bidentate nitrate [31].



M = Co, Complex (2)
M = Ni, Complex (3)

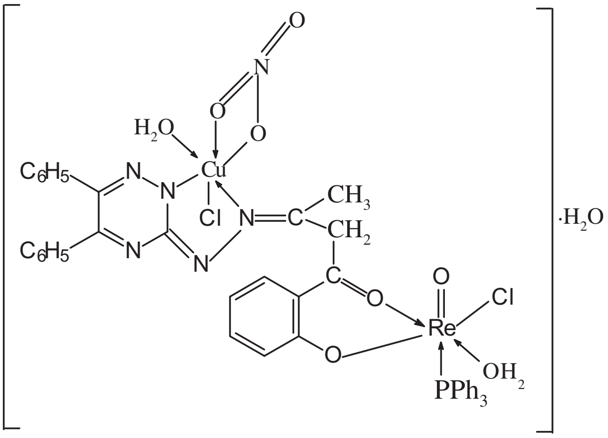


M = Co, Complex (9)
M = Ni, Complex (10)

FIGURE 3 Structures of heteronuclear complexes of oxorhenium(V) and Co(II) and Ni(II) ions, obtained by using the mole ratio 1:1 of complex ligand **a** or **b** to cobalt or nickel ions. (**2**) Aquachloronitratocobalt(II) [aquachlorotriphenylphosphine-1(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-yl-hydrazone)oxorhenium(V)] monohydrate complex(**9**) Aquachloronitratocobalt(II) [aquachlorotriphenylphosphine-1-(2- hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)oxorhenium(V)] monohydrate complex. (**3**) Aquachloronitratonickel(II)[aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone)oxorhenium(V)] monohydrate complex. (**10**) Aquachloronitratonickel(II)[Aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)oxorhenium(V)] monohydrate complex.

The bands observed in the heteronuclear complexes at 360–367 cm^{-1} are assigned to νRe–Cl, while the new bands in the range 341–349 cm^{-1}, which are observed in all complexes except **7** and **14**, may be assigned to heterometal–chlorine bonds.

The heteronuclear complexes showed bands at 308–311 cm^{-1} and 535–695 cm^{-1}, assigned to νM–P and νM–O, respectively. The first band was observed in the spectra of the complex ligands, indicating that the triphenylphosphine is still coordinated to the rhenium ion. Also, new bands were observed at 425–479 cm^{-1} in the heteronuclear complexes, due to the bonds between the heterometal cation and the nitrogen atoms, while these bands were not observed in the complex ligands.



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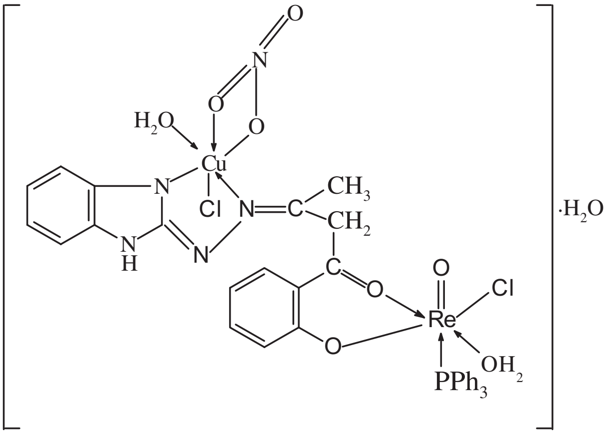


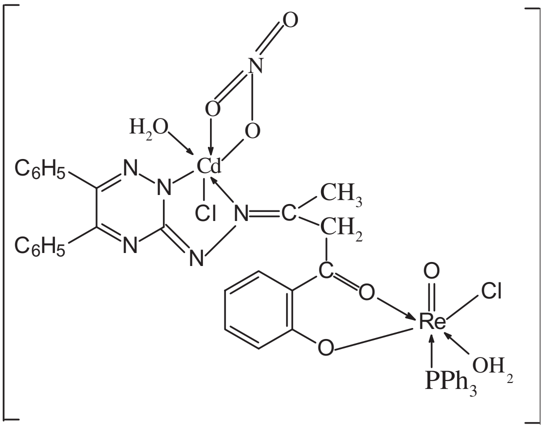
(11)

FIGURE 4 Structures of the heteronuclear complexes of oxorhenium(V) and Cu(II), obtained by using the mole ratio 1:1 of complex ligand **a** or **b** to copper ion. (**4**) Aquachloronitratocopper(II)[aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone) oxorhenium(V)] monohydrate complex. (**11**) Aquachloronitratocopper(II)[aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)oxorhenium(V)] monohydrate complex.

Conductivity Measurements

Conductivity measurements, Table III, indicated that Complexes **1**, **7**, **8** and **14** are 1:1, 1:2, 1:1 and 1:2 electrolytes, respectively, while the other complexes are nonelectrolytes. The colors of solutions of the dissolved complexes did not change during or after measurements. Also, the lower values of the molar conductance of the nonelectrolytic complexes indicate that Cl^- was not replaced by DMF molecules.

The chloride ions in Complexes **7** and **14** were detected by adding a solution of $AgNO_3$, confirming the electrolytic nature of these complexes. The relatively low values of the measured conductivity of the electrolytes may be due to the bulky cations which contain the ReO(V) ion(s) and the heterometal ion.



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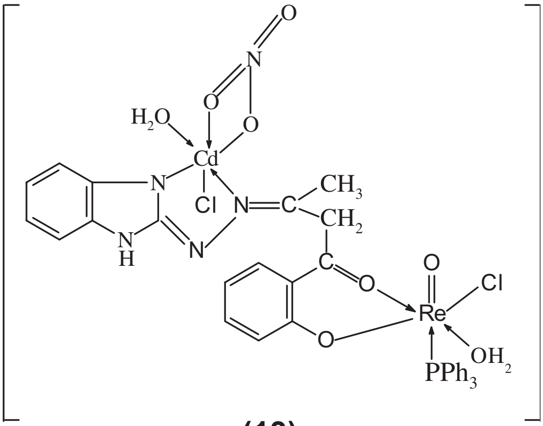


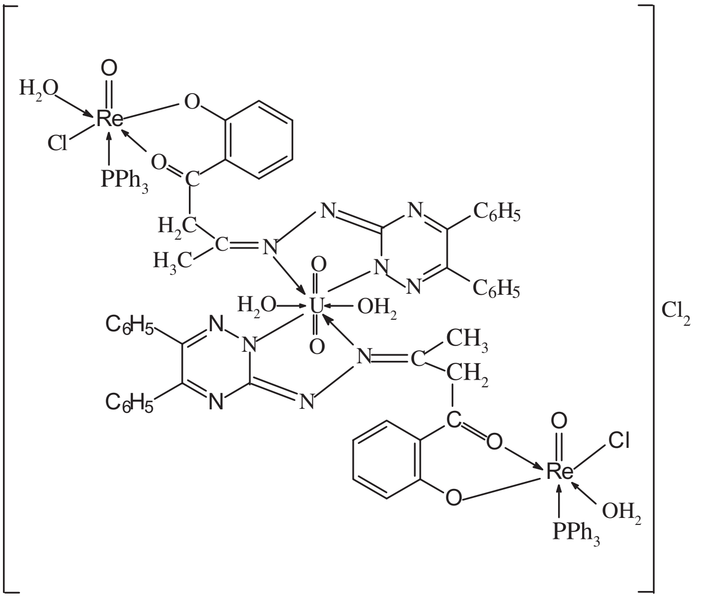
(13)

FIGURE 5 Structures of the heteronuclear complexes of oxorhenium(V) and Cd(II), obtained by using the mole ratio 1:1 of complex ligands **a** or **b** to the cadmium ion. (**6**) Aquachloronitratocadmium(II)[aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone) oxorhenium(V)] complex. (**13**) Aquachloronitratocadmium(II)[aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)oxorhenium(V)] complex.

Nuclear Magnetic Resonance Spectral Studies

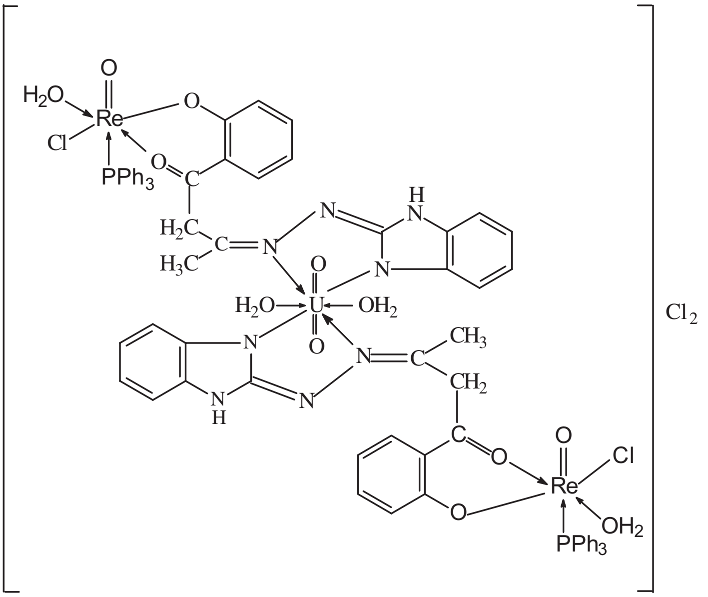
The assignment of the main signals in the ^{1}H NMR spectra of the complex ligands and their diamagnetic heterometal complexes are listed in Table III. The spectra of Complexes **13** and **14** show signals due to NH(ring) at δ 9.41 ppm (1H) and δ 9.46 ppm (2H), respectively, similar to their positions in the corresponding complex ligand at δ 9.48 ppm (1H).

The signal corresponding to the NH^8 group appears at δ 10.08 ppm (1H) and δ 9.80 ppm (1H) in complex ligands **a** and **b**, respectively. In Complexes **6**, **7**, **13** and **14** this signal disappeared owing to complexation with the heterometal cation. The protons of the methylene group (CH$_2$^{5}) were observed at δ 2.52 ppm (2H) for both complex ligands and were unaffected in all heterometal complexes.



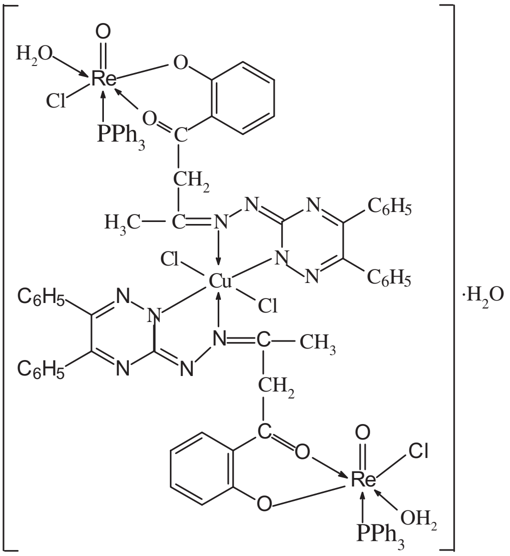
(7)

FIGURE 6 Structure of the heteronuclear complex of oxorhenium(V) and UO_2(VI), obtained by using the mole ratio 1:1 of complex ligand **a** to uranyl ion. (**7**) Diaquadioxouranium(VI) bis[aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone)oxorhenium(V)]dichloride complex.



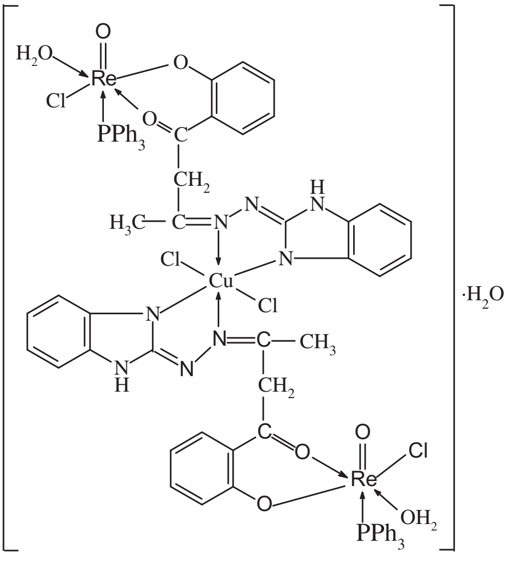
(14)

FIGURE 7 Structure of the heteronuclear complex of oxorhenium(V) and UO_2(VI), obtained by using the mole ratio of complex ligand **b** to uranyl ion. (**14**) Diaquadioxouranium(VI) bis[aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)oxorhenium(V)] dichloride complex.



(5)

FIGURE 8 Structure of the heteronuclear complex of oxorhenium(V) and Cu(II), obtained by using the mole ratio 2:1 of complex ligand **a** to copper ion. (**5**) Dichlorocopper(II) bis[aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(5,6-diphenyl-1,2,4-triazine-3-ylhydrazone)oxorhenium(V)]monohydrate complex.



(12)

FIGURE 9 Structure of the heteronuclear complex of oxorhenium(V) and Cu(II), obtained by using the mole ratio 2:1 of complex ligand **b** to copper ion. (**12**) Dichlorocopper(II)bis[aquachlorotriphenylphosphine-1-(2-hydroxyphenyl)butane-1,3-dione-3-(1*H*-benzimidazol-2-ylhydrazone)oxorhenium(V)] monohydrate complex.

TABLE I Analytical and physical data for the complex ligands $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$, $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$ and their heterobinuclear complexes

Compound	*Color*	*Yield (%)*	*Elemental Analyses Found (Calcd.)*						
			C	*H*	*N*	*P*	*Re*	*M*	*Cl*
a $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$ $C_{43}H_{37}N_5O_4Cl_2PRe$ M.Wt. 975.89	Dark greenish blue	70	52.64 (52.92)	3.95 (3.82)	7.10 (7.18)	3.00 (3.17)	19.20 (19.08)	–	7.10 (7.26)
1 $[ReO(L^1)(PPh_3)(OH_2)ClFe(NO_3)(OH_2)Cl]NO_{3.}\cdot H_2O$ $C_{43}H_{40}N_7O_{12}Cl_2PReFe$ M.Wt. 1190.76	Chocolate brown	69	43.53 (43.37)	3.48 (3.38)	8.00 (8.23)	2.40 (2.60)	15.52 (15.64)	4.30 (4.69)	5.93 (5.95)
2 $[ReO(L^1)(PPh_3)(OH_2)ClCo(NO_3)(OH_2)Cl]\cdot H_2O$ $C_{43}H_{40}N_6O_9Cl_2PReCo$ M.Wt. 1131.84	Dark green	74	45.93 (45.63)	3.76 (3.56)	7.20 (7.42)	2.60 (2.74)	16.29 (16.45)	5.04 (5.21)	6.30 (6.26)
3 $[ReO(L^1)(PPh_3)(OH_2)ClNi(NO_3)(OH_2)Cl]\cdot H_2O$ $C_{43}H_{40}N_6O_9Cl_2PReNi$ M.Wt. 1131.60	Green	70	45.70 (45.64)	3.50 (3.56)	7.33 (7.43)	2.60 (2.74)	16.48 (16.45)	5.00 (5.19)	6.14 (6.26)
4 $[ReO(L^1)(PPh_3)(OH_2)ClCu(NO_3)(OH_2)Cl]\cdot H_2O$ $C_{43}H_{40}N_6O_9Cl_2PReCu$ M.Wt. 1136.46	Grayish green	73	44.99 (45.44)	3.48 (3.55)	7.20 (7.39)	2.50 (2.72)	16.26 (16.38)	5.37 (5.59)	6.10 (6.24)
5 $\{[ReO(L^1)(PPh_3)(OH_2)Cl]_2CuCl_2\}\cdot H_2O$ $C_{86}H_{74}N_{10}O_9Cl_4P_2Re_2Cu$ M.Wt. 2031.32	Brown	76	50.74 (50.85)	3.76 (3.67)	6.70 (6.89)	3.00 (3.05)	18.40 (18.33)	2.98 (3.13)	6.84 (6.98)
6 $[ReO(L^1)(PPh_3)(OH_2)ClCd(NO_3)(OH_2)Cl]$ $C_{43}H_{38}N_6O_8Cl_2PReCd$ M.Wt. 1167.31	Brown	72	43.99 (44.24)	3.48 (3.28)	7.00 (7.20)	2.62 (2.65)	15.87 (15.95)	9.47 (9.63)	6.15 (6.07)

7 $\{[ReO(L^1)(PPh_3)(OH_2)Cl]_2UO_2(OH_2)_2\}Cl_2$ $C_{86}H_{76}N_{10}O_{12}Cl_4P_2Re_2U$ M.Wt. 2255.81	Reddish brown	70	46.02 (45.79)	3.37 (3.39)	6.00 (6.21)	2.80 (2.75)	16.60 (16.51)	10.30 (10.55)	6.30 (6.29)
b $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$ $C_{35}H_{32}N_4O_4Cl_2PRe$ M.Wt. 860.75	Pale green	69	48.48 (48.84)	3.91 (3.75)	6.40 (6.51)	3.45 (3.60)	21.60 (21.63)	–	8.30 (8.24)
8 $[ReO(HL^2)(PPh_3)(OH_2)ClFe(NO_3)(OH_2)Cl]NO_3 \cdot H_2O$ $C_{35}H_{35}N_6O_{12}Cl_2PReFe$ M.Wt. 1075.63	Brown	65	38.92 (39.08)	3.25 (3.28)	7.70 (7.81)	2.60 (2.88)	17.24 (17.31)	5.30 (5.19)	6.48 (6.59)
9 $[ReO(HL^2)(PPh_3)(OH_2)ClCo(NO_3)(OH_2)Cl] \cdot H_2O$ $C_{35}H_{35}N_5O_9Cl_2PReCo$ M.Wt. 1016.71	Green	66	41.08 (41.35)	3.70 (3.47)	6.80 (6.89)	2.90 (3.05)	18.27 (18.31)	5.90 (5.80)	6.84 (6.97)
10 $[ReO(HL^2)(PPh_3)(OH_2)ClNi(NO_3)(OH_2)Cl] \cdot H_2O$ $C_{35}H_{35}N_5O_9Cl_2PReNi$ M.Wt. 1016.47	Light green	67	41.20 (41.36)	3.53 (3.47)	6.65 (6.89)	2.90 (3.05)	18.19 (18.32)	5.90 (5.77)	6.93 (6.97)
11 $[ReO(HL^2)(PPh_3)(OH_2)ClCu(NO_3)(OH_2)Cl] \cdot H_2O$ $C_{35}H_{35}N_5O_9Cl_2PReCu$ M.Wt. 1021.32	Green	70	41.30 (41.16)	3.62 (3.45)	6.70 (6.86)	2.80 (3.03)	18.20 (18.23)	6.05 (6.22)	6.72 (6.94)
12 $\{[ReO(HL^2)(PPh_3)(OH_2)Cl]_2CuCl_2\} \cdot H_2O$ $C_{70}H_{64}N_8O_9Cl_4P_2Re_2Cu$ M.Wt. 1801.05	Green	71	46.32 (46.68)	3.60 (3.58)	6.00 (6.22)	3.30 (3.44)	20.53 (20.68)	3.34 (3.53)	7.72 (7.87)
13 $[ReO(HL^2)(PPh_3)(OH_2)ClCd(NO_3)(OH_2)Cl]$ $C_{35}H_{33}N_5O_8Cl_2PReCd$ M.Wt. 1052.17	Gray	72	39.80 (39.95)	3.00 (3.16)	6.70 (6.66)	2.70 (2.94)	17.58 (17.70)	10.52 (10.68)	6.80 (6.74)
14 $\{[ReO(HL^2)(PPh_3)(OH_2)Cl]_2UO_2(OH_2)_2]\}Cl_2$ $C_{70}H_{66}N_8O_{12}Cl_4P_2Re_2U$ M.Wt. 2025.54	Lemon green	72	41.60 (41.51)	3.40 (3.28)	5.46 (5.53)	3.00 (3.06)	18.26 (18.39)	11.60 (11.75)	6.85 (7.00)

TABLE II Characteristic IR bands (cm^{-1})^a of the complex ligands [ReO(HL^1)(PPh$_3$)(OH$_2$)Cl]Cl, [ReO(H$_2$L^2)(PPh$_3$)(OH$_2$)Cl]Cl and their heterobinuclear complexes

Compound	*νNH^8*	*νNH (ring)*	*νCO*	*νC=N^7*	*νCN (ring) and νCN^8*	*νReO*	*νM–O*	*νM–N*	*νM–Cl*	*νM–P*	*Additional bands*
a	3128m	–	1662 m	1588 m	1530 s	997 s	684 m, 637 w, 617 m	–	359 m	312 m	3508 br (coordinated water)
1	–	–	1658 m	1562 m	1526 m	1002 s	695 m, 642 m, 621 w, 600 m, 581 m	469 m, 431 m	362 m, 346 m	310 m	3504 br (coordinated water), 3368 br (lattice water), 1439 s, 1386 m, 1212 s and 819 w (bidentate chelating NO_3^- group), 1369 s and 828 w (ionic nitrate)
2	–	–	1654 m	1556 m	1528 m	1000 s	694 m, 643 m, 616 w, 583 m, 535 m	457 m, 426 m	364 m, 342 m	308 m	3478 br (coordinated water), 3365 br (lattice water), 1439 s, 1384 m, 1223 m and 813 w (bidentate chelating NO_3^- group)
3	–	–	1654 m	1562 m	1529 m	999 s	693 m, 640 m, 617 w, 584 m, 538 m	457 m, 426 m	364 m, 347 m	310 m	3505 br (coordinated water), 3358 br (lattice water), 1438 s, 1386 m, 1223 m and 812 w (bidentate chelating NO_3^- group)
4	–	–	1667 m	1561 m	1528 m	999 s	693 m, 644 w, 619 m, 588 w, 540 m	471 m, 426 m	367 m, 345 m	309 m	3506 br (coordinated water), 3368 br (lattice water), 1438 s, 1380 s, 1218 m and 805 w (bidentate chelating NO_3^- group)
5	–	–	1670 m	1542 m	1526 m	999 s	693 m, 629 w, 587 m	458 m, 426 m	362 m, 349 m	311 m	3366 br (lattice water)
6	–	–	1656 m	1562 m	1524 m	1000 s	694 m, 643 w, 615 w, 585 m, 37 m	452 m, 428 m	365 m, 342 w	308 m	3508 br (coordinated water), 1439 s, 1384 m, 1224 m and 812 w (bidentate chelating NO_3^- group)

7	–	–	1666 m	1559 m	1523 m	998 s	692 m, 639 w, 616 w, 538 m	461 m, 441 m	364 m	311 m	3486 br (coordinated water), 922 s (antisymmetric ν_3 O=U=O)
b	3159 m	3119 m	1651 m	1580 m	1516 s	997 s	693 s, 637 w, 619 m	–	365 m	310 m	3502 br (coordinated water)
8	–	3122 m	1646 m	1542 m	1512 m	997 s	692 s, 634 w, 605 m, 582 w, 541 s	468 m, 425 w	361 m, 347 m	310 m	3508 br (coordinated water), 3360 br (lattice water), 1436 s, 1385 m, 1216 m and 814 w (bidentate chelating NO_3^- group), 1373 s and 829 w (ionic nitrate)
9	–	3122 m	1653 m	1545 m	1517 m	997 s	692 s, 638 w, 618 w, 587 w, 546 s	473 w, 449 m	361 m, 343 m	308 m	3506 br (coordinated water), 3347 br (lattice water), 1436 s, 1388 m, 1201 s and 830 w (bidentate chelating NO_3^- group)
10	–	3120 m	1650 m	1549 m	1515 m	998 s	694 s, 636 w, 619 m, 583 w, 545 s	468 w, 431 m	362 m, 345 m	310 m	3506 br (coordinated water), 3383 br (lattice water), 1437 s, 1384 m, 1213 m and 818 w (bidentate chelating NO_3^- group)
11	–	3123 m	1647 m	1558 m	1516 m	998 s	693 s, 639 w, 620 m, 587 w, 549 s	479 m, 430 m	363 m, 341 m	308 m	3509 br (coordinated water), 3365 br (lattice water), 1437 s, 1376 s, 1214 m and 817 w (bidentate chelating NO_3^- group)
12	–	3119 m	1656 m	1544 m	1516 m	997 s	693 s, 635 w, 619 m, 578 w, 548 s	476 w, 430 m	364 m, 345 m	310 m	3505 br (coordinated water), 3354 br (lattice water)
13		3121 m	1652 m	1544 m	1520 m	996 s	693 s, 638 w, 620 m, 593 m, 542 s	468 w, 434 m	364 m, 341 w	310 m	3493 br (coordinated water), 1436 s, 1386 m, 1227 m and 819 w (bidentate chelating NO_3^- group)
14	–	3121 m	1656 m	1547 m	1515 m	997 s	691 s, 639 w, 617 w, 540 s	472 w, 449 m	360 m	310 m	3505 br (coordinated water), 920 s (antisymmetric ν_3O=U=O)

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

TABLE III Physical measurements of the complex ligands $[ReO(HL^1)(PPh_3)(OH_2)Cl]Cl$, $[ReO(H_2L^2)(PPh_3)(OH_2)Cl]Cl$ and their heterobinuclear complexes

Compound	*Molar conductance*[a] *(*$Ohm^{-1}\,cm^2\,mol^{-1}$*)*	μ_{eff}[b] *(BM)*	λ_{max}[a] *(nm)*	δNH^8	δNH *(ring)*	$\delta CH_2{}^5$	δH_2O *(Coordinated)*	δH_2O *(Lattice)*
a	54	0.07	243, 295, 324, 346, 597	10.08 (1 H)	–	2.52 (2 H)	3.45 (2 H)	–
1	48	5.56	240, 298, 327, 342, 506, 593, 714	*	*	*	*	*
2	6	4.59	248, 290, 329, 352, 473, 562, 599	*	*	*	*	*
3	11	2.94	244, 287, 331, 360, 426, 589, 704	*	*	*	*	*
4	14	1.86	248, 290, 323, 343, 592, 637	*	*	*	*	*
5	9	1.78	243, 282, 314, 349, 583, 622	*	*	*	*	*
6	7	0.05	240, 287, 326, 348, 448	–	–	2.49 (2 H)	3.48 (4 H)	–
7	93	0.08	248, 296, 321, 352, 516	–	–	2.51 (4 H)	3.52 (8 H)	–
b	45	0.06	288, 307, 380, 530	9.80 (1 H)	9.48 (1 H)	2.52 (2 H)	3.46 (2 H)	–
8	52	5.64	283, 304, 388, 503, 533, 704	*	*	*	*	*
9	9	4.54	286, 311, 376, 462, 527, 574	*	*	*	*	*
10	7	2.97	279, 308, 382, 423, 535, 709	*	*	*	*	*
11	12	1.92	284, 308, 372, 538, 643	*	*	*	*	*
12	10	1.75	276, 301, 369, 534, 631	*	*	*	*	*
13	7	0.06	284, 314, 380, 439	–	9.41 (1 H)	2.54 (2 H)	3.49 (4 H)	–
14	98	0.11	288, 316, 393, 528	–	9.46 (2 H)	2.52 (4 H)	3.44 (8 H)	–

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

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

[c] Chemical shifts relative to TMS.

[*] Not carried out due to their paramagnetism.

TABLE IV Thermal analysis of the heteronuclear complexes

Compound	*Temperature range (°C)*	*Loss in weight Actual (Calcd.) (%)*	*DSC peak (°C)*		*ΔH (J/g)*	*Composition of residue*	*Probable composition of expelled groups*
			Endo	*Exo*			
1	40–97	1.56 (1.51)	89	–	16.84	$[ReO(L^1)(PPh_3)(OH_2)ClFe(NO_3)(OH_2)Cl]NO_3$	One molecule of lattice water
	97–186	4.58 (4.54)	162	–	86.38	$[ReO(L^1)(PPh_3)ClFe(NO_3)Cl]NO_3$	Two molecules of coordinated water
	186–314	15.82 (15.70)	2889	–	62.56	$[ReO(L^1)(PPh_3)Fe(NO_3)]$	One molecule of Cl_2 and one molecule of NO_3
	314–627	43.30 (42.93)	–	405	−68.84	$[ReO(L^1)Fe]$	One molecule of NO_3 and one molecule of PPh_3
2	40–93	1.68 (1.59)	86	–	14.36	$[ReO(L^1)(PPh_3)(OH_2)ClCo(NO_3)(OH_2)Cl]$	One molecule of lattice water
	93–208	4.81 (4.77)	164	–	13.91	$[ReO(L^1)(PPh_3)ClCo(NO_3)Cl]$	Two molecules of coordinated water
	208–453	39.88 (39.69)	–	283	−15.66	$[ReO(L^1)Co]$	One molecule of Cl_2, one molecule of NO_3 and one molecule of PPh_3
3	35–82	1.60 (1.59)	76	–	12.52	$[ReO(L^1)(PPh_3)(OH_2)ClNi(NO_3)(OH_2)Cl]$	One molecule of lattice water
	82–197	4.85 (4.77)	183	–	20.38	$[ReO(L^1)(PPh_3)ClNi(NO_3)Cl]$	Two molecules of coordinated water
	197–445	39.94 (39.70)	–	256	−24.89	$[ReO(L^1)Ni]$	One molecule of Cl_2, one molecule of NO_3 and one molecule of PPh_3
4	40–86	1.64 (1.58)	78	–	10.77	$[ReO(L^1)(PPh_3)(OH_2)ClCu(NO_3)(OH_2)Cl]$	One molecule of lattice water
	86–167	4.98 (4.75)	163	–	120.96	$[ReO(L^1)(PPh_3)ClCu(NO_3)Cl]$	Two molecules of coordinated water
	167–358	39.84 (39.53)	–	239	−35.71	$[ReO(L^1)Cu]$	One molecule of Cl_2, one molecule of NO_3 and one molecule of PPh_3
5	35–98	0.96 (0.89)	77	–	17.94	$\{[ReO(L^1)(PPh_3)(OH_2)Cl]_2CuCl_2\}$	One molecule of lattice water
	98–167	2.80 (2.66)	143	–	11.43	$\{[ReO(L^1)(PPh_3)Cl]_2CuCl_2\}$	Two molecules of coordinated water
	167–365	34.90 (34.58)	–	256	−44.63	$\{[ReO(L^1)]_2Cu\}$	Two molecule of Cl_2 and two molecules of PPh_3
6	70–189	3.25 (3.09)	163	–	11.41	$[ReO(L^1)(PPh_3)ClCd(NO_3)Cl]$	Two molecules of coordinated water
	189–408	37.28 (36.94)	–	257	−27.35	$[ReO(L^1)Cd]$	One molecule of Cl_2, one molecule of NO_3 and one molecule of PPh_3
7	85–256	3.24 (3.19)	242	–	20.43	$\{[ReO(L^1)(PPh_3)Cl]_2UO_2\}Cl_2$	Four molecules of coordinated water
	256–387	32.94 (32.73)	–	254	−29.65	$\{[ReO(L^1)]_2UO_2\}$	Two molecules of Cl_2 and two molecules of PPh_3
8	40–94	1.74 (1.67)	83	–	28.47	$[ReO(HL^2)(PPh_3)(OH_2)ClFe(NO_3)(OH_2)Cl]NO_3$	One molecule of lattice water
	94–181	5.18 (5.02)	159	–	75.32	$[ReO(HL^2)(PPh_3)ClFe(NO_3)Cl]NO_3$	Two molecules of coordinated water
	181–324	17.60 (17.38)	293	–	72.45	$[ReO(HL^2)(PPh_3)Fe(NO_3)]$	One molecule of Cl_2 and one molecule of NO_3
	324–593	47.91 (47.53)	–	408	−52.73	$[ReO(HL^2)Fe]$	One molecule of NO_3 and one molecule of PPh_3
9	40–96	1.85 (1.77)	92	–	28.34	$[ReO(HL^2)(PPh_3)(OH_2)ClCo(NO_3)(OH_2)Cl]$	One molecule of lattice water
	96–198	5.53 (5.31)	166	–	15.72	$[ReO(HL^2)(PPh_3)ClCo(NO_3)Cl]$ $[ReO(HL^2)Co]$	Two molecules of coordinated water
	198–437	44.43 (44.16)	–	297	−19.36		One molecule of Cl_2, one molecule of NO_3 and one molecule of PPh_3

(*continued*)

TABLE IV Continued

Compound	*Temperature range (°C)*	*Loss in weight Actual (Calcd.) (%)*	*DSC peak (°C)*		*ΔH (J/g)*	*Composition of residue*	*Probable composition of expelled groups*
			Endo	*Exo*			
10	35–87	1.84 (1.77)	52	–	14.91	$[ReO(HL^2)(PPh_3)(OH_2)ClNi(NO_3)(OH_2)Cl]$	One molecule of lattice water
	87–179	5.50 (5.32)	176	–	23.71	$[ReO(HL^2)(PPh_3)ClNi(NO_3)Cl]$	Two molecules of coordinated water
	179–443	44.38 (44.20)	–	305	−52.90	$[ReO(HL^2)Ni]$	One molecule of Cl_2, one molecule of NO_3 and one molecule of PPh_3
11	35–92	1.88 (1.76)	78	–	14.32	$[ReO(HL^2)(PPh_3)(OH_2)ClCu(NO_3)(OH_2)Cl]$	One molecule of lattice water
	92–144	5.35 (5.29)	137	–	40.68	$[ReO(HL^2)(PPh_3)ClCu(NO_3)Cl]$	Two molecules of coordinated water
	144–439	44.09 (43.99)	–	226	−162.66	$[ReO(HL^2)Cu]$	One molecule of Cl_2, one molecule of NO_3 and one molecule of PPh_3
12	40–89	1.17 (1.00)	72	–	36.28	$\{[ReO(HL^2)(PPh_3)(OH_2)Cl]_2CuCl_2\}$	One molecule of lattice water
	89–176	3.22 (3.00)	161	–	49.34	$\{[ReO(HL^2)(PPh_3)Cl]_2CuCl_2\}$	Two molecules of coordinated water
	176–374	40.32 (40.00)	–	294	−37.25	$\{[ReO(HL^2)]_2Cu\}$	Two molecules of Cl_2 and two molecules of PPh_3
13	65–188	3.47 (3.42)	154	–	32.78	$[ReO(HL^2)(PPh_3)ClCd(NO_3)Cl]$	Two molecules of coordinated water
	188–426	41.26 (40.98)	–	273	−28.36	$[ReO(HL^2)Cd]$	One molecule of Cl_2, one molecule of NO_3 and one molecule of PPh_3
14	80–234	3.62 (3.56)	196	–	47.34	$\{[ReO(HL^2)(PPh_3)Cl]_2UO_2\}Cl_2$	Four molecules of coordinated water
	234–392	36.68 (36.46)	–	267	−36.42	$\{[ReO(HL^2)]_2UO_2\}$	Two molecules of Cl_2 and two molecules of PPh_3

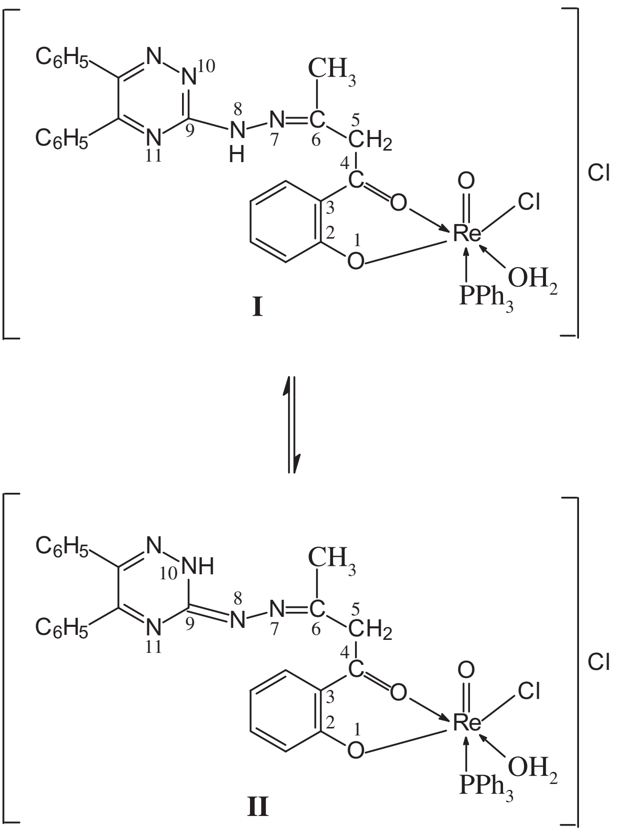


FIGURE 10 Tautomeric structures of complex ligand **a**.

Complexes **6**, **7**, **13** and **14** also showed a resonance due to coordinated water molecules in the range 3.44–3.52 ppm [32]. The existence of the coordinated water molecules in the complexes was further confirmed by thermal analyses.

From the ^{1}H NMR and IR spectra, we suggest that the mode of coordination of the complex ligands **a** and **b** is monoanionic bidentate through the nitrogen atom (N^{10}) of the heterocyclic ring and the nitrogen atom of the $C{=}N^7$ group.

Thermal Analyses

The results of TG-DSC analyses of the heterometal complexes are shown in Table IV, showing good agreement with the formulas suggested from the analytical data, Table I.

The loss of the water of crystallization from the heterometal complexes, except Complexes **6**, **7**, **13** and **14**, occurs in the temperature range 82–98°C. Elimination of lattice water was accompanied by an endothermic peak with $\Delta H = 10.77$–36.28 J/g.

The coordinated water molecules were eliminated from the heterometal complexes at relatively higher temperatures (144–256°C) in comparison with the crystal water molecules. This process was accompanied by an endothermic peak with $\Delta H = 11.41$–120.96 J/g.

The elimination of Cl_2, NO_3 and PPh_3 from the heterometal complexes occurred at temperatures $> 314°C$. It was obvious that the elimination of a PPh_3 molecule from the heteronuclear complexes was accompanied by an exothermic peak with $\Delta H = -15.66$ to $+162.66$ J/g. Although this process led to nonisolable complexes, it can be attributed to a change in geometry around the oxorhenium cation.

Electronic Spectra and Magnetic Moments of the Complexes

The magnetic measurement data and the values of λ_{max} are presented in Table III and Fig. 12.

Complex ligand **a** shows five absorption bands at 243, 295, 324, 346 and 597 nm, and complex ligand **b** shows four absorption bands at 228, 307, 380 and 530 nm. The electronic absorption spectra of the heterometal complexes **1**–**5** and **8**–**12** show similar bands to the complex ligands. These bands are consistent with ligand field electronic transitions nd→σ^*d and nd→π^*d, usually observed for metal complexes with 4–5d^2 electronic configurations [33,34]. Also, new visible bands were observed for the heterometal complexes which may be assigned either to charge-transfer or d→d transitions through the heterometal ions.

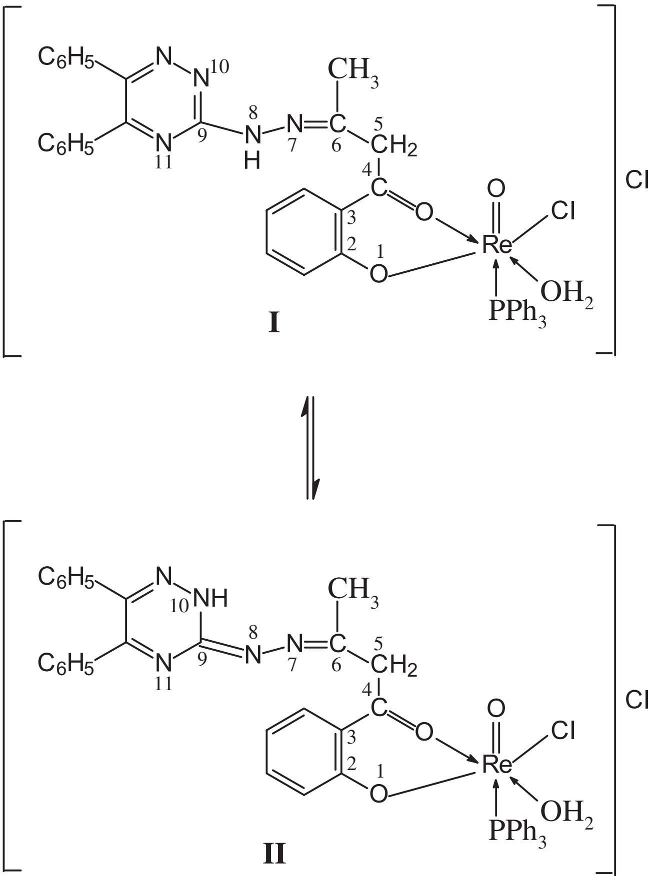


FIGURE 11 Tautomeric structures of complex ligand **b**.

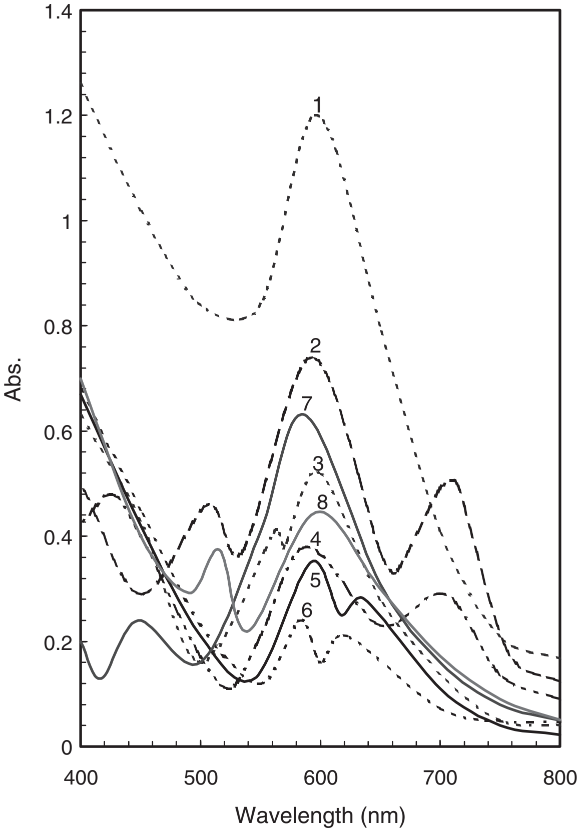


FIGURE 12 Visible spectra of: 1, complex ligand **a**; 2, $[ReO(L^1)(PPh_3)(OH_2)ClFe(NO_3)(OH_2)Cl]NO_3 \cdot H_2O$ (**1**); 3, $[ReO(L^1)(PPh_3)(OH_2)ClCo(NO_3)(OH_2)Cl] \cdot H_2O$ (**2**); 4, $[ReO(L^1)(PPh_3)(OH_2)ClNi(NO_3)(OH_2)Cl] \cdot H_2O$ (**3**); 5, $[ReO(L^1)(PPh_3)(OH_2)ClCu(NO_3)(OH_2)Cl] \cdot H_2O$ (**4**); 6, $\{[ReO(L^1)(PPh_3)(OH_2)Cl]_2 CuCl_2\} \cdot H_2O$ (**5**); 7, $[ReO(L^1)(PPh_3)(OH_2)ClCd(NO_3)(OH_2)Cl]$ (**6**); and 8, $[ReO(L^1)(PPh_3)(OH_2)Cl]_2UO_2(OH_2)_2\}Cl_2$ (**7**).

The electronic spectra of heteronuclear complexes **1** and **8** of Fe(III), showed two new bands at 503–506 nm and 704–714 nm, which are assigned to the $^6A_{1g} \rightarrow {}^4A_1$, $^4E(G)$ and $^6A_1 \rightarrow {}^4T_2(G)$ transitions. These spectral data and the magnetic moment (5.56–5.64 BM) are comparable with those reported for octahedral geometry around the Fe(III) ion [35,36]. The proposed structures of Complexes **1** and **8** are shown in Fig. 2.

The heteronuclear complexes of Co(II), **2** and **9,** have magnetic moments in the range (4.54–4.59 BM) which agrees well with the expected value for a high-spin Co(II) ion in an octahedral environment. The electronic spectra of the Co(II) complex showed two new bands at 462–473 and 562–574 nm, which are assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions, respectively. The ν_1 transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ is expected to appear at lower frequency (beyond 1000 nm) and hence was not observed, while the observed transitions are consistent with octahedral geometry [37–39]. The proposed structures of Complexes **2** and **9** are shown in Fig. 3.

The magnetic moment values of the heteronuclear Ni(II) complexes **3** and **10** are 2.94 and 2.97 BM, respectively, suggesting their octahedral structure [40]. The visible spectra of the heteronuclear Ni(II) complexes showed new bands in the region 423–426 and 704–709 nm, which are assignable to the electronic transitions $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(P)$, respectively. The proposed structures of Complexes **3** and **10** are also shown in Fig. 3.

The magnetic moment values of the heteronuclear Cu(II) Complexes **4**, **5**, **11** and **12** are 1.75–1.92 BM. These values are slightly higher than the spin value (1.73 BM) expected for one unpaired electron, which offers the possibility of an octahedral geometry around Cu(II) ions [41]. The electronic spectra of these complexes exhibit new bands at 637, 622, 643 and 631 nm, respectively, assigned to the $^2E_g\rightarrow{}^2T_{2g}$ transition, considering octahedral geometry [42,43]. The proposed structures of Complexes **4** and **11** are shown in Fig. 4, and those for Complexes **5** and **12** are shown in Figs. 8 and 11, respectively.

The electronic spectra of the diamagnetic heteronuclear complexes **6** and **13** of Cd(II) exhibit absorption bands at 448 and 439 nm, respectively. Also, the heteronuclear Complexes **7** and **14** of UO_2(VI) exhibit absorption bands at 516 and 528 nm, respectively. The bands observed may be due to overlap between the nd$\rightarrow\sigma^*$d and nd$\rightarrow\pi^*$d electronic transitions and charge transfer from the complex ligand to the heterocations. The suggested structures of Cd(II) Complexes **6** and **13** are six-coordinate and have an octahedral configuration as shown in Fig. 5. The suggested structures of the heteronuclear complexes **7** and **14** of UO_2(VI) are eight-coordinate, i.e., distorted dodecahedral geometry, Figs. 6 and 7, respectively. The IR spectrum of the unusual eight-coordinate UO_2(VI) complexes shows a strong band at 922 cm^{-1} for the former and at 920 cm^{-1} for the latter, assigned to the antisymmetric ν_3(OUO) vibration [44].

ESR Spectra

X-band electron spin resonance (ESR) spectra of heteronuclear complexes **4** and **11** are shown in Fig. 13. The spectra show two anisotropic signals ($g_1 = 2.25$, 2.02) and ($g_{11} = 2.11$, 2.00). The values of g_{eff} for these complexes are more positive than the free electron, $g = 2.0023$, due to an apparently higher covalent character in the bonding between the complex ligand and copper(II) ions [45]. The shape of the ESR spectra together with the g_{eff} values indicate distorted octahedral geometry around Cu(II) [46,47]. The ESR spectral data of the heteronuclear complexes of Cu(II) thus support the previous magnetic results.

Antifungal Activities

Complex ligands **a** and **b** and their heterometal complexes were tested against the fungal species *Alternaria alternata* and *Aspergillus niger*. Some antibiotics were also evaluated for their antifungal activities and their results are compared with those of the complex ligands and their heterometal complexes. The results are cited in Tables V and VI.

All heteronuclear Complexes **1**–**14** and the complex ligands **a** and **b** have activity towards *Alternaria alternata* and *Aspergillus niger*. The comparison of their biological activities is based on comparing the diameter of inhibition zone (mm)/mol and revealed the following:

(1) Heterometal Complexes **1**–**7** showed higher activities towards *Alternaria alternata* than complex ligand **a**.

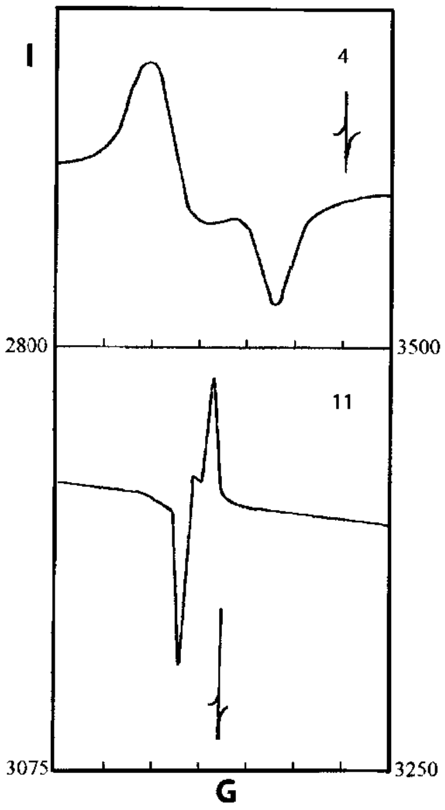


FIGURE 13 ESR powder spectra; X-bands, of: $[ReO(L^1)(PPh_3)(OH_2)ClCu(NO_3)(OH_2)Cl] \cdot H_2O$ (**4**) and $[ReO(HL^2)(PPh_3)(OH_2)ClCu(NO_3)(OH_2)Cl] \cdot H_2O$ (**11**) complexes.

TABLE V Antifungal activities of complex ligands **a** and **b** and their heteronuclear complexes

Compound	*Diameter of inhibition zone (mm)/mol*[a]	
	Alternaria alternata	*Aspergillus niger*
a	185	342
1	381	321
2	443	352
3	284	204
4	318	284
5	833	612
6	338	256
7	880	773
b	362	353
8	581	538
9	488	469
10	275	163
11	296	194
12	1117	1018
13	684	663
14	1479	1408

[a] 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)/mol*	
	Alternaria alternata	*Aspergillus niger*
Ampicillin	132	140
Ultrafen	187	201
Dalacin C	73	87
Flumox	138	122
Unasyn	113	71
Cefradine	42	51
Doxymycin	25	29
Septrin	15	18

(2) Complex ligand **a** shows higher activities towards *Aspergillus niger* than Complexes **1**, **3**, **4** and **6**.

(3) Heterometal complexes of complex ligand **b** showed higher activities than those of complex ligand **a** toward both *Alternaria alternata* and *Aspergillus niger* except Complexes **10** and **11**.

(4) Complex ligand **b** and its heterometal complexes are generally more active than complex ligand **a** and its heterometal complexes.

(5) Trinuclear Complexes **5**, **7**, **12** and **14** showed much higher activities than mono- and dinuclear metal complexes.

(6) The activities of the dinuclear complexes of complex ligand **a** follow the sequence: Co(II) > Fe(III) > Cu(II) ~ Cd(II) > Ni(II). The activity of its trinuclear complexes showed that UO_2(VI) > Cu(II).

(7) The activity of dinuclear complexes of complex ligand **b** follows the sequence: Cd(II) > Fe(III) > Co(II) > Cu(II) > Ni(II). The activity of its trinuclear complexes showed that UO_2(VI) > Cu(II).

Comparison of the biological activities of the complex ligands and their heterometal complexes with some known antibiotics revealed that these compounds are biologically active. In some cases, the tested complexes even have higher activities than the antibiotics tested. These results may draw more attention to the possible use of these complexes in medical treatment.

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