

A study of the effect of ammonia gas on the solid mono- and dinuclear oxorhenium(V) complexes

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The reaction of ammonia gas with the solid oxorhenium(V) complexes $[\text{Re}_2\text{O}_3\text{L}_2\text{Cl}_4] \cdot 2\text{H}_2\text{O}$, $[\text{Re}_2\text{O}_2\text{L}_3\text{Cl}_6] \cdot 2\text{H}_2\text{O}$, $[\text{ReOLCl}(\text{OH}_2)_3]\text{Cl}_2$, $[\text{ReOL}_2(\text{OH}_2)_3]\text{Cl}_3$, $[\text{ReOLCl}_3(\text{OH}_2)]$, $[\text{ReOL}(\text{SCN})_2\text{Cl}(\text{OH}_2)] \cdot \text{H}_2\text{O}$ and $[\text{ReOL}(\text{SCN})\text{Cl}_2(\text{OH}_2)]$ (where $\text{L} = 2\text{-benzimidazolethione}$), yielded the corresponding ammine and/or amine complexes, $[\text{Re}_2\text{O}_3\text{L}_2(\text{NH}_3)_2(\text{NH}_2)_2]\text{Cl}_2$ (**I**), $[\text{Re}_2\text{O}_2\text{L}_3(\text{NH}_3)_2(\text{NH}_2)_4]\text{Cl}_2$ (**II**), $[\text{Re}_2\text{O}_3\text{L}_2(\text{NH}_3)_2(\text{NH}_2)_4] \cdot \text{H}_2\text{O}$ (**III**), $[\text{Re}_2\text{O}_3\text{L}_4(\text{NH}_2)_4]$ (**IV**), $[\text{Re}_2\text{O}_3\text{L}_2(\text{NH}_3)_2(\text{NH}_2)_4]$ (**V**), $[\text{Re}_2\text{O}_3\text{L}_2(\text{SCN})_4(\text{NH}_3)_2]$ (**VI**) and $[\text{Re}_2\text{O}_3\text{L}_2(\text{Thio})_2(\text{NH}_2)_4]$ (**VII**), respectively, (Thio = thiourea) where ammonia gas has replaced other ligands such as chlorine and water. In complex **VII** thiourea replaced the thiocyanate group in the start complex through its reaction with ammonia gas. The obtained ammine and/or amine of rhenium(V) complexes have been observed to decompose through several isolatable, as well as non-isolatable complex species as intermediates during heating. $[\text{Re}_2\text{O}_3\text{L}_4]$, $[\text{Re}_2\text{O}_3\text{L}_2(\text{NH}_2)_4]$ and $[\text{Re}_2\text{O}_3\text{L}_2(\text{SCN})_4]$, were synthesized pyrolytically in the solid state from the corresponding parent oxorhenium complexes. The electronic absorption spectra and magnetic moments of the complexes show that the Re(V) cation has an octahedral configuration. IR, $^1\text{H-NMR}$ spectroscopy, conductivity measurements and thermal analysis show that ammonia and thiourea behave as neutral monodentate ligands, SCN^- and NH_2^- as monodentate monoanionic ligands, the organic ligand (L) as a neutral monodentate or bidentate ligand towards the metal cation.

Key words: ammine and amine complexes, synthesis, magnetic properties, electrical conductivity, $^1\text{H-NMR}$, thermal analysis.

In preceding communications¹⁻⁴ the synthesis and characterization of complexes of oxorhenium(V) with Lewis base ligands (O, N and/or S -donors) were reported. In continuation of this work, the oxorhenium(V) complexes of 2-benzimidazolethione³ and mixed thiocyanate-2-benzimidazolethione⁴ were treated with ammonia gas to form different octahedral complexes. The ammonia displaces the coordinated chloride or water ligands by ammine and/or amine ligands. Ammonia gas reacts with the thiocyanate ligand in the parent complex $[\text{ReOL}(\text{SCN})\text{Cl}_2(\text{OH}_2)]$ to form thiourea which coordinates to the rhenium cation through the sulfur atom of the $\text{C}=\text{S}$ group. The mononuclear complexes are converted through treatment

with ammonia gas into dinuclear complexes. The possibility of obtaining some new oxorhenium(V) complexes pyrolytically in the solid state, which cannot be synthesized from solution and/or from gas solid interaction, was investigated by thermal analysis. Benzimidazole derivatives have antiinflammatory activity⁵⁻⁹ and other biological activities,¹⁰⁻¹² such as antibacterial, antiviral and anthelmintic. The interaction of ammonia with complexes which contain 2-benzimidazolthione may lead to complexes with peculiar biological properties.

This paper describes the synthesis of different ammine and/or amine oxorhenium (V) complexes, the investigation of the thermal decomposition behaviour of these complexes and the isolation of possible intermediate products formed upon heating.

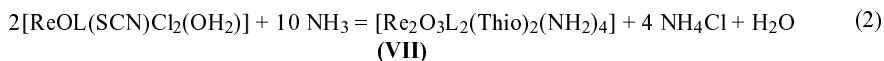
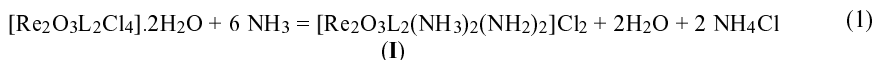
EXPERIMENTAL

Materials

The parent oxorhenium complexes were prepared according to literature methods.^{3,4} Ammonia gas was generated by heating a mixture of solid NH_4Cl and NaOH , and dried over NaOH pellets. Ethanol, DMF, 1,4-dioxane, acetone, chloroform, ether, HCl and DMSO were reagent grade chemicals.

Preparation of ammine and/or amine oxorhenium complexes

The complexes were prepared by passing NH_3 gas over the solid parent oxorhenium(V) complexes for two hours, then kept in a vacuum desiccator over conc. H_2SO_4 for one day to remove adsorbed ammonia gas. Ammonia gas was repassed over the products to insure their complete reaction, they were then stored in a vacuum desiccator. The complexes **I-VII** were washed with ethanol, then ether and dried in vacuum desiccator over KOH for two days. They were soluble in DMF, DMSO , partially soluble in EtOH and insoluble in chloroform and 1,4-dioxane. The following equations illustrate examples of the formation of different ammine and/or amine oxorhenium(V) complexes:



Physical measurements and analyses

Electronic spectra of solutions of the complexes in DMF were recorded on a JASCO model V-550 UV/VIS spectrophotometer. IR spectra were recorded on a Perkin-Elmer 598 spectrometer using KBr discs, polystyrene was used as a calibrant. Far-infrared spectra were measured with a Nicolet 20 FTIR spectrometer using polyethylene discs. Magnetic measurements were carried out by the Gouy method at room temperature using a Johnson Matthey Alfa products, Model No. MKI, magnetic susceptibility balance using $\text{Hg}[\text{Co}(\text{CNS})_4]$ as a calibrant. Diamagnetic corrections were calculated from Pascal's constants.¹³ TG-DTA measurements were carried out on SHIMADZU thermogravimetric analyzer using TA-50 WSI program. Conductivities were measured on solutions of the complexes in DMF (10^{-3} M) using a Wissenschaftlich-Technische werkstätten, D 8120 Weilheim, Germany, Model LBR 40A, conductivity meter. ^1H -NMR spectra ($\text{DMSO}-d_6$) were recorded at room temperature on a cryomagent for NMR spectroscopy 200 MHz/52 MM, a product of Spectrospin and Bruker using TMS as internal standard. Microanalyses for carbon, hydrogen, nitrogen and sulfur were carried out at the microanalytical center, Cairo University, Giza, Egypt. Rhenium and chlorine were determined gravimetrically as nitron perrhenate and silver chloride,¹⁴ respectively.

RESULTS AND DISCUSSION

The parent oxorhenium(V) complexes of the ligand 2-benzimidazolethione,³ Fig. 1, and thiocyanate-12-benzimidazolethione,⁴ Figs. 2 and 3, had been previously prepared and characterized. The reaction of ammonia gas with solid dinuclear or mononuclear oxorhenium(V) complexes yielded a variety of dinuclear ammine and/or amine oxorhenium(V) complexes, whereby the starting mononuclear complexes are converted into dinuclear ones. The isolated ammine and/or amine oxorhenium(V) complexes were amorphous solids upon removal of the solvent. Characterization of the solid complexes was carried out by chemical analyses, IR, visible, ¹H-NMR spectra, thermal analysis, magnetic and conductivity measurement (Tables I-V).

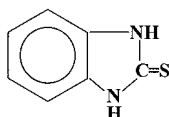


Fig. 1. Structure of the ligand, 2-benzimidazolethione, abbreviated as $\begin{smallmatrix} \text{NH} \\ | \\ \text{C}=\text{S} \end{smallmatrix}$

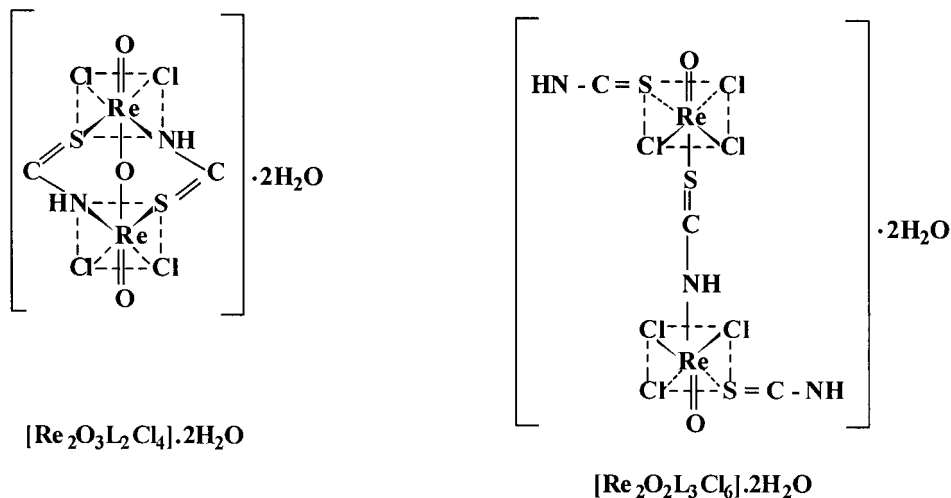


Fig. 2. Structures of the parent dinuclear oxorhenium(V) complexes.

IR Spectra

The IR spectra of the solid ligand (2-benzimidazolethione) and its ammine and/or amine oxorhenium(V) complexes are listed in Table III. The complexes I-VII, Fig. 4, showed bands at 1270–1279 cm^{-1} due to coordinated C=S which are shifted to lower wave numbers in comparison with that of the free ligand (L). The involvement of the C=S group in the coordination was also confirmed by the appearance of a band at 295–308 cm^{-1} due to $\nu(\text{Re}-\text{S})$, which is in agreement with the previously reported values for rhenium(V)-sulfur bonded compounds.²⁻⁴ For complex VII bands appeared at 1222 and 290 cm^{-1} due to $\nu(\text{C}=\text{S})$ and $\nu(\text{Re}-\text{S})$, respectively, of thiourea which is coordinated through the thione group.² The

stretching vibration of different N–H bonds in complexes **I–VII** were observed at different wave numbers. The ν (NH) of uncoordinated benzimidazolethione was observed at $3165 - 3170 \text{ cm}^{-1}$. The ν of coordinated benzimidazolethione was observed at $3138 - 3147 \text{ cm}^{-1}$, ν (NH) of the NH_2 group was observed at $3103 - 3110 \text{ cm}^{-1}$ and ν (NH) of NH_3 at $3070 - 3083 \text{ cm}^{-1}$. Also, a band was observed at 3385 cm^{-1} in the case of complex **VII** due to the stretching vibration of the uncoordinated amino group of thiourea. The participation of the NH groups in the coordination was confirmed by the appearance of bands at $415 - 480 \text{ cm}^{-1}$ due to ν (Re–N).¹⁵ The thiocyanate group in complex **VI** has a strong band at 2078 cm^{-1} which indicated

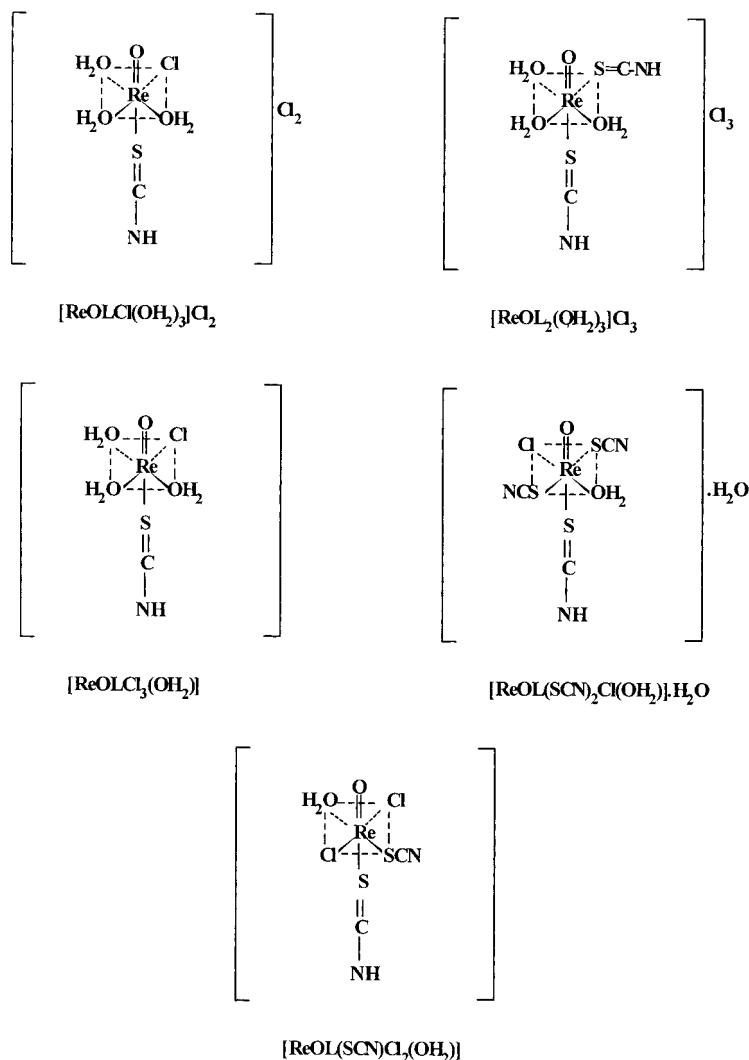


Fig. 3. Structures of the parent mononuclear oxorhenium(V) complexes.

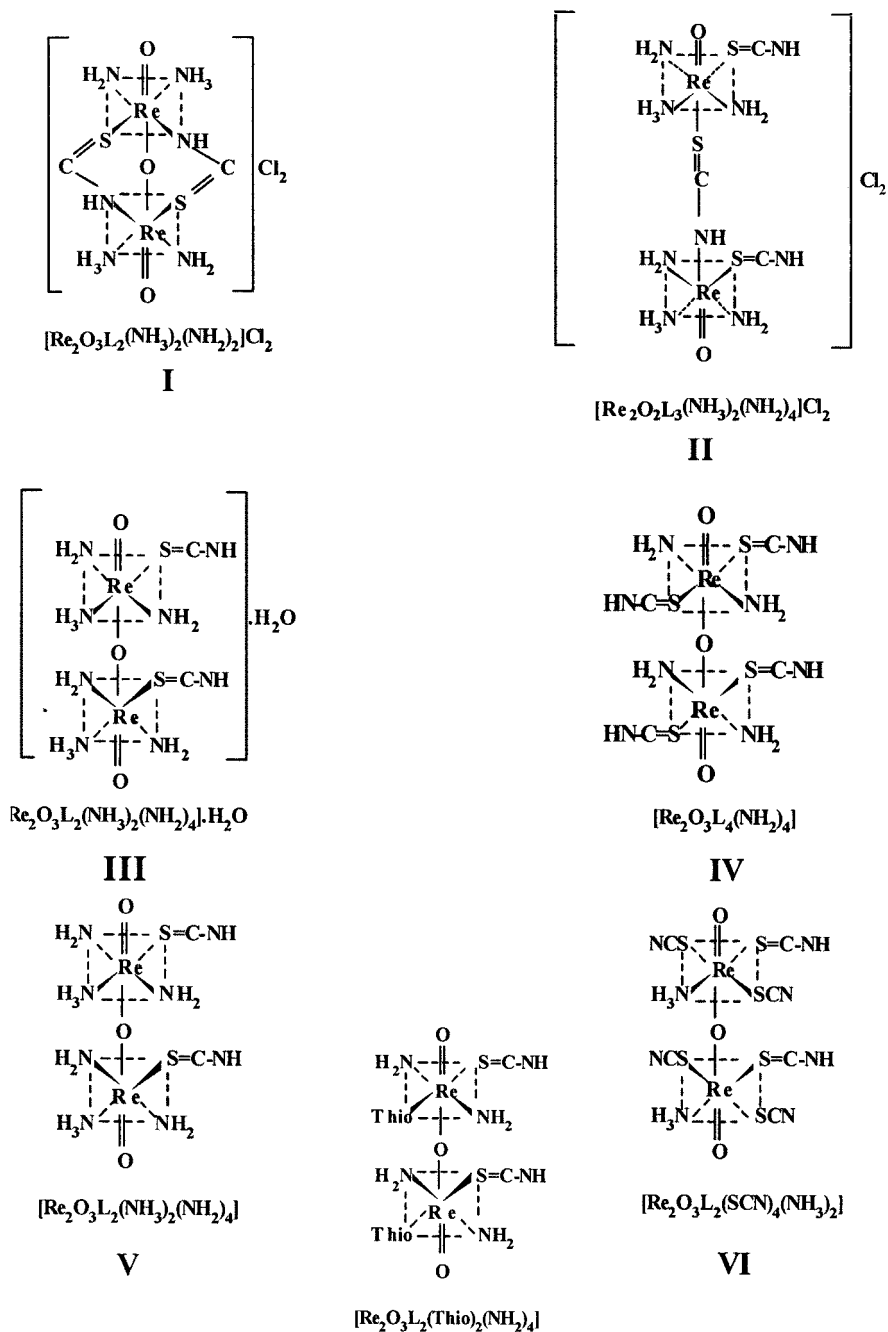


Fig. 4. Structures of ammine and/or amine oxorhenium(V) complexes.

its participation in complexation *via* the sulfur atom.^{2,4,14} All complexes exhibit strong bands at 916–920 cm⁻¹ due to $\nu(\text{Re}=\text{O})$ of dinuclear rhenium complexes and at 708–715 cm⁻¹ due to $\nu_{\text{as}}(\text{Re}-\text{O}-\text{Re})$, which is consistent with the values cited in the literature for other similar dinuclear complexes.²⁶⁻²⁰ The presence of more than one band for either $\nu(\text{Re}-\text{N})$ or $\nu(\text{Re}-\text{S})$ indicates the presence of more than one ammine and/or amine or thiocyanate group, complex **VI**, respectively.

UV-visible spectra

The UV spectrum of 2-benzimidazolethione shows an absorption band at 270 nm. The ammine and/or amine complexes exhibit two or three bands, Table II. The absorption in the range 300–425 nm was assigned to the $d\pi(\text{Re}) \rightarrow \pi^*$ (ligand) transition and the absorption in the range 200–300 nm was assigned to intraligand $\pi \rightarrow \pi^*$ transition.²¹

TABLE I. Elemental analyses of the ammine and/or amine oxorhenium (V) complexes

| Compound | Decomp. °C | Colour | Yield % | Found (Calc.)% | | | | | |
|--|---------------|--------------------|------------|------------------|----------------|------------------|------------------|------------------|----------------|
| | | | | C | H | N | S | Re | Cl |
| I. [Re ₂ O ₃ L ₂ (NH ₃) ₂ (NH ₂) ₂]Cl ₂ | >320 | green | 60 | 19.30 (19.58) | 2.47 (2.56) | 13.00 (13.05) | 7.30 (7.46) | 43.20 (43.41) | 8.10 (8.27) |
| II [Re ₂ O ₂ L ₃ (NH ₃) ₂ (NH ₂) ₄]Cl ₂ | >335 | deep green | 70 | 24.45 (24.60) | 3.00 (3.12) | 16.30 (16.40) | 9.00 (9.37) | 36.20 (36.37) | 6.70 (6.93) |
| III. [Re ₂ O ₃ L ₂ (NH ₃) ₂ (NH ₂) ₄].H ₂ O | >270 | deep brown | 70 | 19.80 (20.07) | 3.00 (3.11) | 16.50 (16.73) | 7.30 (7.65) | 44.30 (44.50) | – |
| IV [Re ₂ O ₃ L ₄ (NH ₂) ₄] | > 290 | brown | 65 | 30.70 (30.96) | 3.00 (2.95) | 15.30 (15.48) | 11.70 (11.79) | 34.20 (34.32) | – |
| V [Re ₂ O ₃ L ₂ (NH ₃) ₂ (NH ₂) ₄] | > 300 | brown | 60 | 20.40 (20.52) | 3.20 (3.17) | 17.00 (17.10) | 7.90 (7.81) | 45.25 (45.48) | – |
| VI [Re ₂ O ₃ L ₂ (SCN) ₄ (NH ₃) ₂] | > 280 | reddish- brown | 60 | 21.60 (21.89) | 1.90 (1.82) | 14.00 (14.18) | 19.30 (19.45) | 37.60 (37.74) | – |
| VII [Re ₂ O ₃ L ₂ (Thio) ₂ (NH ₂) ₄] | > 320 | brownish -black | 65 | 20.35 (20.49) | 2.70 (2.99) | 17.80 (17.93) | 13.40 (13.66) | 39.70 (39.75) | – |

Magnetic moments

The complexes of oxorhenium(V) were all diamagnetic.²² The magnetic moments of the dinuclear ammine and/or amine rhenium(V) complexes, Table II, confirm their diamagnetic character.

Conductivity measurements

Conductivity measurements, Table II, showed that complexes **III**, **IV**, **V**, **VI** and **VII** are non-electrolytes while complexes **I** and **II** are 1 : 2 electrolytes.

Nuclear magnetic resonance spectral studies

The main signals in the $^1\text{H-NMR}$ spectra of 2-benzimidazolethione and its ammine and/or amine complexes are listed in Table IV. The free ligand 2-benzimidazolethione showed a signal at δ 11.87 ppm (2H) assigned to the NH of the imidazole ring. The signal of the uncoordinated NH group in complexes **I–VII** was slightly shifted downfield (11.92–12.24). While the signal of coordinate the NH group, as in complex **I** and **II**, is shifted downfield (13.25, 13.47) due to strong deshielding by the metal cation. The amine group showed signals ranging between 7.0–7.26 ppm and the ammine group in the range 3.48–3.67. In complex **VII**, the signals of the NH_2 group of thiourea are observed at δ 9.87 ppm due to the non-participation of its NH_2 groups in complexation.²

TABLE II. Physicochemical measurements of the ligand, 2-benzimidazolethione, and its ammine and/or amine oxorhenium(V) complexes

| Compound | Molar conductance ^a /ohm ⁻¹ cm ² mol ⁻¹ | μ_{eff} ^a /B.M. | λ_{max} ^b /nm |
|---|---|---------------------------------------|---|
| C ₇ H ₆ N ₂ S (ligand L) | — | — | 270 |
| I | 98 | 0.06 | 295,400sh |
| II | 87 | 0.11 | 299,410sh |
| III | 7.2 | 0.07 | 297,405sh |
| IV | 16.3 | 0.14 | 298,350sh,405sh |
| V | 12.4 | 0.12 | 295,340sh,395sh |
| VI | 4.5 | 0.07 | 281.5,375,425sh |
| VII | 5.2 | 0.15 | 285.5,405sh |

^aMeasurements were taken at 27 °C. ^bDMF solutions, 1×10^{-3} M at 25 °C.

TABLE III. Characteristic IR bands (cm⁻¹)^a of 2-benzimidazolethione and its ammine and/or amine oxorhenium(V) complexes

| Compound | $\nu(\text{NH})$ | $\nu(\text{C}=\text{S})$ | $\nu(\text{Re}=\text{O})$ | $\gamma(\text{CH})$ ^b | $\nu(\text{Re}-\text{N})$ | $\nu(\text{Re}-\text{S})$ | Additional bands |
|---|-----------------------------|--------------------------|---------------------------|----------------------------------|---------------------------|---------------------------|--|
| C ₇ H ₆ N ₂ S(L) | 3165b | 1340s | — | 740s | — | — | — |
| I | 3170b,3143m, 3107m,3072m | 1275m | 916s | 743s | 480m,445m, 420w | 305m | 714m, $\nu_{\text{as}}(\text{Re}-\text{O}-\text{Re})$ |
| II | 3170b,3140m, 3110m,3083m | 1276m | 917s | 743s | 477m,440w, 419m | 308m | — |
| III | 3165b,3108m, 3079m | 1275m | 917s | 750s | 473m,438w, 415m | 307m | 708m, $\nu_{\text{as}}(\text{Re}-\text{O}-\text{Re})$ 3420b(lattice water) |
| IV | 3170b,3103m | 1276m | 917s | 747s | 478m,442w, 423m | 295m | 712m, $\nu_{\text{as}}(\text{Re}-\text{O}-\text{Re})$ |

TABLE III. *contd.*

| Compound | $\nu(\text{NH})$ | $\nu(\text{C}=\text{S})$ | $\nu(\text{Re}=\text{O})$ | $\gamma(\text{CH})^b$ | $\nu(\text{Re}-\text{N})$ | $\nu(\text{Re}-\text{S})$ | Additional bands |
|------------|--|----------------------------------|---------------------------|-----------------------|---|-----------------------------|--|
| V | 3165 <i>b</i> , 3105 <i>m</i> , 3070 <i>m</i> | 1275 <i>m</i> | 917 <i>s</i> | 743 <i>s</i> | 472 <i>m</i> , 437 <i>w</i> , 417 <i>m</i> | 305 <i>m</i> | 709 <i>m</i> , $\nu_{\text{as}}(\text{Re}-\text{O}-\text{Re})$ |
| VI | 3170 <i>b</i> , 3080 <i>m</i> | 1270 <i>m</i> | 920 <i>s</i> | 747 <i>s</i> | 484 <i>m</i> , 442 <i>m</i> | 312 <i>m</i> , 295 <i>w</i> | 715 <i>m</i> , $\nu_{\text{as}}(\text{Re}-\text{O}-\text{Re})$, 2078 <i>s</i> $\nu(\text{SCN})$ |
| VII | 3385 <i>b</i> , 3165 <i>b</i> , 3107 <i>m</i> | 1279 <i>m</i> , 1222 <i>m</i> | 917 <i>s</i> | 747 <i>s</i> | 473 <i>m</i> , 438 <i>m</i> | 308 <i>m</i> , 290 <i>w</i> | 710 <i>m</i> , $\nu_{\text{as}}(\text{Re}-\text{O}-\text{Re})$ |

^a*b* = broad, *s* = strong, *m* = medium, and *w* = weak, ^b $\gamma(\text{CH})$ of 4 adjacent H-phenyl atoms.

Thermal analyses

The thermal decomposition products of the complexes are tabulated in Table V. Almost all the complexes lose first either HCl, NH₃ or H₂O endothermally, then they lose ligand molecules exothermally whereby the coordination geometry of the metal changes. Elimination of either HCl or thiourea molecules corresponds to deprotonation of the ligand 2-benzimidazolethione which would be coordinated to the metal cation as a bidentate monocharged anion, as in complexes **I**, **II** and **VII**. The loss of NH₃ gas would change the ligand 2-benzimidazolethione from a monodentate to either a neutral bidentate, as in complexes **III**, **V** and **VI**, or bidentate monocharged anion, as in complex **IV**.

TABLE IV. The ¹H-NMR chemical shifts of 2-benzimidazolethione ligand and its ammine and/or amine oxorhenium(V) complexes

| Compound | $\delta\text{NH}(\text{Ligand})$ Uncoordinated | $\delta\text{NH}(\text{Ligand})$ Coordinated | δNH_2 Amine | δNH_3 Ammine |
|--|---|---|---------------------------------|----------------------------|
| C ₇ H ₆ N ₂ S(ligand L) | 11.87(2H) | — | — | — |
| I | 11.94(2H) | 13.25(2H) | 7.05(4H) | 3.48(6H) |
| II | 12.08(5H) | 13.47(1H) | 7.12(8H) | 3.57(6H) |
| III | 12.02(4H) | — | 7.00(8H) | 3.52(6H) |
| IV | 12.24(8H) | — | 7.26(8H) | — |
| V | 12.07(4H) | — | 7.06(8H) | 3.54(6H) |
| VI | 11.92(4H) | — | — | 3.67(6H) |
| VII | 11.95(4H) | — | 7.23(8H) 9.87 [*] (8H) | — |

^{*} δ of NH₂ - Thiourea.

Pyrolytical preparation of oxorhenium(V) complexes and their characterization

New rhenium(V) complexes were prepared pyrolytically from the parent complexes **IV**, **{V, VII}** and **VI**. The structures of the obtained products are discussed on the basis of their IR spectra, conductivity measurements, ¹H-NMR and elemental analysis for rhenium and sulphur.

[Re₂O₃L₄]: This complex was prepared by heating complex **IV** at 260 °C to constant weight upon which a black product was obtained. Its IR spectrum showed bands assigned to $\nu(\text{Re}=\text{O})$ at 915 cm^{-1} and $\nu(\text{Re}-\text{O}-\text{Re})$ at 708 cm^{-1} , which confirms that the complex is present in the dimeric form.^{20,22} The IR spectrum also showed the disappearance of the band at 3103 cm^{-1} due to $\nu(\text{NH}_2)$ of the amine groups. The intensity of the band due to $\nu(\text{NH})$ of the imidazole ring, 3170 cm^{-1} decreased. Besides, new bands appeared at 485 and 464 cm^{-1} due to $\nu(\text{Re}-\text{N})$. The band due to $\nu(\text{C}=\text{S})$ of the ligand appeared at 1279 cm^{-1} . These results indicate that the ligand had changed from a neutral monodenatate to a monocharged bidentate anion. Furthermore, its ¹H-NMR spectrum showed a signal at δ 12.16 (4H) of the uncoordinated proton of the NH groups of imidazole rings and the disappearance of the signal at δ 7.26 (8H) of the amine groups. Conductivity measurements in DMF solution proved that it is a non-electrolyte. From the previous results and elemental analyses for rhenium and sulphur, the thermal product could be represented as *[Re₂O₃L₄]* and its proposed structure is given in Fig. 5.

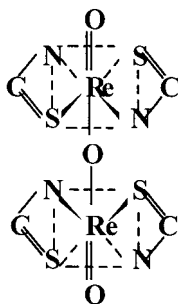


Fig. 5. Proposed structure of *[Re₂O₃L₄]* obtained by heating complex **IV** at 260 °C.

TABLE V. Thermal decomposition of ammine and/or amine oxorhenium(V) complexes

| Complex | Temp. °C | % Weight loss TG data Found (Calcd) | DTA peak Endo or exo | Probable composition of expelled molecules | Suggested composition of the thermolysis products |
|------------|----------|---|-------------------------|--|---|
| I | 266 | 8.70(8.51) | endo | 2HCl | Re ₂ O ₃ L ₂ (NH ₃) ₂ (NH ₂) ₂ |
| | 505 | 48.30(47.49) | exo | 2L, 2NH ₃ | Re ₂ O ₃ (NH ₂) ₂ |
| II | 275 | 10.70(10.45) | endo | 2HCl, 2NH ₂ | Re ₂ O ₂ L ₃ (NH ₂) ₄ |
| | 380 | 26.0(25.10) | exo | L | Re ₂ O ₂ L ₂ (NH ₂) ₄ |
| III | 102 | 2.30(2.15) | endo | H ₂ O | Re ₂ O ₃ L ₂ (NH ₃) ₂ (NH ₂) ₄ |
| | 220 | 6.42(6.21) | endo | 2NH ₃ | Re ₂ O ₃ L ₂ (NH ₂) ₄ |
| | 385 | 24.50(24.14) | exo | L | Re ₂ O ₃ L(NH ₂) ₄ |
| IV | 258 | 6.00(6.28) | endo | 4NH ₃ | Re ₂ O ₃ L ₄ |
| | 482 | 32.3(33.91) | exo | 2L | Re ₂ O ₃ L ₂ |

TABLE V. Contd.

| Complex | Temp. °C | % Weight loss TG data Found (Calcd) | DTA peak Endo or exo | Probable composition of expelled molecules | Suggested composition of the thermolysis products |
|------------|----------|---|-------------------------|--|---|
| V | 210 | 4.27(4.15) | endo | 2NH ₃ | Re ₂ O ₃ L ₂ (NH ₂) ₄ |
| | 515 | 40.12(40.79) | exo | 2L | Re ₂ O ₃ (NH ₂) ₄ |
| VI | 195 | 3.50(3.44) | endo | 2NH ₃ | Re ₂ O ₃ L ₂ (SCN) ₄ |
| | 470 | 32.60(33.85) | exo | 2L | Re ₂ O ₃ (SCN) ₄ |
| VII | 225 | 16.40(16.22) | exo | 2Thio | Re ₂ O ₃ L ₂ (NH ₂) ₄ |
| | 481 | 32.52(32.24) | exo | L | Re ₂ O ₃ L(NH ₂) ₄ |

[Re₂O₃L₂(NH₂)₄]: This complex was prepared either by heating complex **V** at 220 °C or complex **VII** at 225 °C to constant weight. The colour of the obtained complex was deep brown and differs from the colours of both parent complexes. Its IR spectrum showed bands assigned to $\nu(\text{Re}=\text{O})$ at 915 cm⁻¹ and to $\nu(\text{Re}-\text{O}-\text{Re})$ at 710 cm⁻¹, which indicate that the thermal product is still present in the dimeric form. The bands due to $\nu(\text{NH}_3)$ in complex **V**, $\nu(\text{NH}_2)$ and $\nu(\text{C}=\text{S})$ of thioruea in complex **VII** disappeared, while a new band was observed at 3128 cm⁻¹ due to the NH group of the imidazole ring being shared in coordination. Besides two new bands appeared at 458 and 443 cm⁻¹ due to $\nu(\text{Re}-\text{N})$. The band corresponding to $\nu(\text{C}=\text{S})$ of 2-benzimidazolethione was observed at 1273 cm⁻¹.

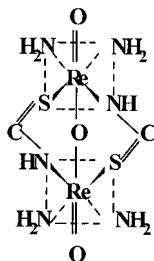


Fig. 6. Proposed structure of [Re₂O₃L₂(NH₂)₄] obtained either by heating complex **V** at 220 °C or complex **VII** at 225 °C.

The ¹H-NMR spectrum showed the disappearance of the signals δ 3.54 (6H), of the NH₃ groups in complex **V** and δ 9.87(8H) of the NH₂ group of the thioruea molecules in complex **VII**, while signals due to the NH group of the imidazole ring were observed at δ 12.03(2H) and δ 13.12(2H). The latter signal is assigned to the coordinated proton of the NH group of the bridged ligand.²

Thus, the IR and ¹H-NMR results indicate that 2-benzimidazolethione acts as a bridging neutral bidentate ligand through the sulphur atom of the C=S group and the nitrogen atom of one of the NH groups of the ring. Conductivity measurements of a DMF solution of the thermal product showed that it is a non-electrolyte. From the previous results and elemental analyses for rhenium and sulphur, the thermal

product could be represented as $[\text{Re}_2\text{O}_3\text{L}_2(\text{NH}_2)_4]$ and its proposed structure is given in Fig. 6.

$[\text{Re}_2\text{O}_3\text{L}_2(\text{SCN})_4]$: This complex prepared by heating complex **VI** at 200 °C to constant weight whereby colour changed from reddish-brown to deep-red. The IR spectrum of the thermal product showed bands at 915 and 708 cm^{-1} due to ν ($\text{Re}=\text{O}$) and ν ($\text{Re}-\text{O}-\text{Re}$), respectively, which indicate that the product is still present in the dimeric form. The band corresponding to $\nu(\text{NH})$ of the coordinated NH group of the imidazole ring was observed at 3135 cm^{-1} . New bands were observed at 462 and 440 cm^{-1} due to $\nu(\text{Re}-\text{N})$. The band corresponding to $\nu(\text{C}=\text{S})$ of 2-benzimidazolethione was observed at 1275 cm^{-1} and the band corresponding to $\nu(\text{SCN})$ appeared at $\approx 2060 \text{ cm}^{-1}$, indicating that the thiocyanate anion is still coordinated *via* its sulphur atom.

The ^1H -NMR spectrum showed the disappearance of the signal δ 3.67(6H) of the NH_3 groups in the parent complex, while signals due to the NH group of imidazole ring were observed at δ 11.96(6H) and δ 13.18(2H). The latter signal is assigned to the coordinated proton of the NH group of the bridged ligand.²

Conductivity measurements in DMF solution showed that the product is a non-electrolyte. From the previous results and elemental analyses for rhenium and sulphur, the thermal product could be represented as $[\text{Re}_2\text{O}_3\text{L}_2(\text{SCN})_4]$ and its proposed structure is given in Fig. 7.

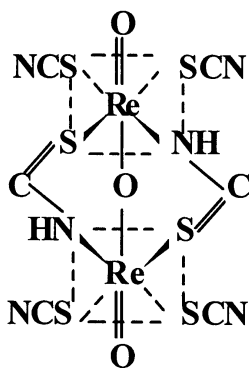
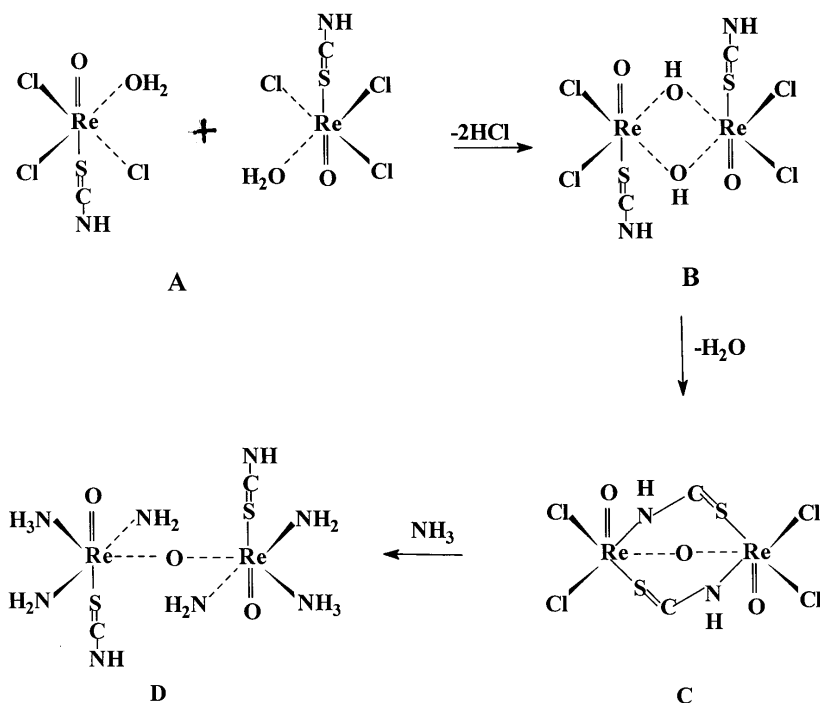


Fig. 7. Proposed structure of $[\text{Re}_2\text{O}_3\text{L}_2(\text{SCN})_4]$, obtained by heating complex **VI** at 200 °C.

CONCLUSION

In conclusion, ammonia gas replaces the chloride ions or water molecules from the coordination sphere of the parent complexes but it cannot replace the organic ligand (L), due to the strong bond between the ligand (L) and the oxorhenium (V) cation. Ammonia reacts with the coordinated SCN group present in the parent complexes to form thiourea. The prepared ammine and/or amine oxorhenium(V) complexes are dinuclear. Thus, the parent mononuclear oxorhenium (V) complexes,



Scheme 1.

Figs. 2 and 3, were converted into dinuclear ones by ammonia gas. The dimerization process can be expressed by the equation shown below for complex **V**, where two molecules of the mononuclear complexes (**A**) lose two molecules of HCl forming the bridged hydroxyoxorhenium moiety (**B**), which leads to oxygen-bridged oxorhenium (**V**) complex (**C**), in which the ligand (**L**) molecules are transferred from monodentate to bridging bidentate ones. Ammonia then reacts with complex (**C**) to form the dinuclear ammine and/or amine oxorhenium(**V**) complex (**D**).

ИЗВОД

ПРОУЧАВАЊЕ УТИЦАЈА ГАСОВИТОГ АМОНИЈАКА НА ЧВРСТЕ МОНО- И
ВИНУКЛЕАРНЕ ОКСОРЕНИЈУМ КОМПЛЕКСЕ

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Реаговањем гасовитог амонијака и чврстих оксоренијум(V) комплекса, $[\text{Re}_2\text{O}_3\text{L}_2\text{Cl}_4] \cdot 2\text{H}_2\text{O}$, $[\text{Re}_2\text{O}_2\text{L}_3\text{Cl}_6] \cdot 2\text{H}_2\text{O}$, $[\text{ReOL}_2(\text{OH}_2)_3]\text{Cl}_2$, $[\text{ReOL}_2(\text{OH}_2)_3]\text{Cl}_3$, $[\text{ReOLCl}_3(\text{OH}_2)]$, $[\text{ReOL}(\text{SCN})_2(\text{OH}_2)] \cdot \text{H}_2\text{O}$ и $[\text{ReOL}(\text{SCN})\text{Cl}_2(\text{OH}_2)]$, (где је L = 2-бензимидазолеион), добијају се одговарајући амонијум или аминок комплекси, $[\text{Re}_2\text{O}_3\text{L}_2(\text{NH}_3)_2(\text{NH}_2)_2]\text{Cl}_2$ (**I**), $[\text{Re}_2\text{O}_2\text{L}_3(\text{NH}_3)_2(\text{NH}_2)]\text{Cl}_2$ (**II**), $[\text{Re}_2\text{O}_3\text{L}_2(\text{NH}_3)(\text{NH}_3)(\text{NH}_2)_4] \cdot \text{H}_2\text{O}$ (**III**), $[\text{Re}_2\text{O}_3\text{L}_4(\text{NH}_2)_4]$ (**IV**), $[\text{Re}_2\text{O}_3\text{L}_2(\text{NH}_3)_2(\text{NH}_2)_4]$ (**V**), $[\text{Re}_2\text{O}_3\text{L}_2(\text{SCN})_4(\text{NH}_3)_2]$ (**VI**) and $[\text{Re}_2\text{O}_3\text{L}_2(\text{Thio})_2(\text{NH}_2)_4]$ (**VII**), респек-

тивно, (Thio = тиоуреа), док је гасовити амонијак заменио друге лиганде, као што су хлор или вода. У комплексу **VII** тиоуреа је заменила тиоцијанатну групу полазног комплекса у реакцији са гасовитим амонијаком. Запажено је да се добијени амонијум и/или аминок комплекси ренијума(V) разлажу на неколике, издвојиве или неиздвојиве врсте као интермедијаре, током грејања. $[\text{Re}_2\text{O}_3\text{L}_4]$, $[\text{Re}_2\text{O}_3\text{L}_2(\text{NH}_2)_4]$ и $[\text{Re}_2\text{O}_3\text{L}_2(\text{SCN})_4]$ су синтетизовани пиролитички у чврстом стању коришћењем матичних орторенијум комплекса. Електронски апсорпциони спектри и магнетни моменти комплекса показују да Re(V) катјон има октаедарску конфигурацију. IR и $^1\text{H-NMR}$ спектроскопија, мерења проводљивости и термичка анализа показује да се амонијак и тиоуреа понашају као неутрални монодентантни лиганди, SCN^- и NH_2^- као монодентантни моноанјонски лиганди, а лиганд (L) као неутрални монодентантни или бидентатни лиганди у односу на метални катјон.

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