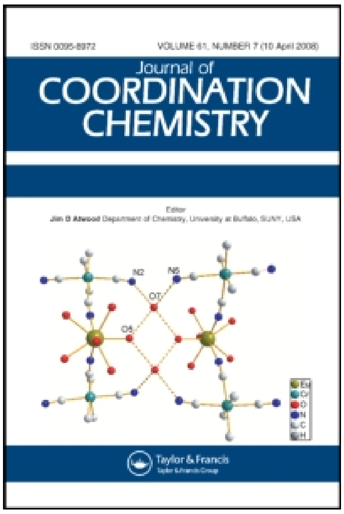

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Characterization of [ReO(Tetramethylthiourea)$_4$](PF$_6$)$_3$ in Solution: Electrochemical, NMR and Ligand Substitution Studies

Dinorah Gambino[a]; Beatriz S. ParajÓn-Costa[b]; Hugo Cerecetto[c]; Mercedes GonzÁlez[d]; Eduardo Kremer[a]; Enrique J. Baran[b]
[a] Cátedra de Química Inorgánica, Facultad de Química, Universidad de la República, Montevideo, Uruguay [b] Centro de Química Inorgánica CEQUINOR/CONICET, UNLP, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina [c] Departamento de Química Orgánica, Facultad de Química, Universidad de la República, Montevideo, Uruguay [d] Laboratorio de Química Orgánica, Facultad de Ciencias, Universidad de la República, Montevideo, Uruguay

To cite this Article Gambino, Dinorah , ParajÓn-Costa, Beatriz S. , Cerecetto, Hugo , GonzÁlez, Mercedes , Kremer, Eduardo and Baran, Enrique J.(2002) 'Characterization of [ReO(Tetramethylthiourea)$_4$](PF$_6$)$_3$ in Solution: Electrochemical, NMR and Ligand Substitution Studies', Journal of Coordination Chemistry, 55: 12, 1441 — 1453

To link to this Article: DOI: 10.1080/00958970210000058835

URL: http://dx.doi.org/10.1080/00958970210000058835

J. Coord. Chem., 2002, Vol. 55, No. 12, pp. 1441–1453

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CHARACTERIZATION OF [ReO(TETRAMETHYLTHIOUREA)$_4$](PF$_6$)$_3$ IN SOLUTION: ELECTROCHEMICAL, NMR AND LIGAND SUBSTITUTION STUDIES

DINORAH GAMBINO[a,*], BEATRIZ S. PARAJÓN-COSTA[d],
HUGO CERECETTO[b], MERCEDES GONZÁLEZ[c],
EDUARDO KREMER[a] and ENRIQUE J. BARAN[d]

[a]*Cátedra de Química Inorgánica;* [b]*Departamento de Química Orgánica, Facultad de Química;*
[c]*Laboratorio de Química Orgánica, Facultad de Ciencias, Universidad de la República,*
C. Correo 1157, 1300-Montevideo, Uruguay; [d]*Centro de Química Inorgánica*
(CEQUINOR/CONICET, UNLP), Facultad de Ciencias Exactas,
Universidad Nacional de La Plata, C. Correo 962, 1900-La Plata, Argentina

(Received 3 August 2001; Revised 6 December 2001; In final form 12 June 2002)

The complex [ReO(Me$_4$tu)$_4$]$^{3+}$, with Me$_4$tu = tetramethylthiourea, is characterized in nonaqueous media. Its structure is studied in acetonitrile solution by ^{1}H and ^{13}C NMR and its electrochemical behavior in the same solvent is analyzed by means of cyclic voltamperometric measurements. Heteronuclear correlation and variable temperature NMR experiments suggest that the complex ion shows a similar structure in solution and in the solid state. At low temperatures (below 0°C) free rotation of the dimethylamine groups around the thiocarbonyl carbon–nitrogen bond is restricted and the dissolved complex adopts the rigid structure observed in the solid state. Cyclic voltamperometric results suggest that the redox behavior of this compound can be explained through an $E_rC_iE_r$ mechanism (a chemical reaction coupled between two electron-transfer reactions). An initial one electron reduction of the complex from Re(V) to Re(IV) followed by an irreversible chemical reaction, leads to a new electroactive species of Re(IV)*, which is reduced to Re(III). The ability of [ReO(Me$_4$tu)$_4$](PF$_6$)$_3$ to serve as a precursor for other Re(V) complexes by ligand substitution is established, in acetone solution, with different kinds of incoming ligands: diethyldithiocarbamate (Et$_2$dtc), ethylenediamine (en) and pyridine (py). The previously known complexes [Re$_2^V$O$_3$(Et$_2$dtc)$_4$], [Re^{V}O$_2$(en)$_2$](PF$_6$) and [Re^{V}O$_2$(py)$_4$](PF$_6$) are easily synthesized under mild conditions with high yields.

Keywords: Oxorhenium(V); Tetramethylthiourea; Cyclic voltammetry; NMR; Ligand substitution

INTRODUCTION

Ligand substitution onto suitable precursors is an important route for the synthesis of Re complexes. This synthetic route relies on labile Re species as preparative intermediates. Thiourea and its alkylated derivatives show low thermodynamic stabilities towards substitution and are easily substituted under mild conditions [1–3]. Previous experimental work indicated [TcO(Me$_4$tu)$_4$](PF$_6$)$_3$, where Me$_4$tu is tetramethylthiourea,

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*Corresponding author. Fax: 5982 9241906. E-mail: dgambino@bilbo.edu.uy

ISSN 0095-8972 print: ISSN 1029-0389 online © 2002 Taylor & Francis Ltd
DOI: 10.1080/0095897021000058835

as a potential synthetic precursor for monooxo and dioxo Tc(V) complexes [4]. $[ReO(Me_4tu)_4]^{3+}$ has been previously characterized and its molecular structure in the solid state has been determined by X-ray diffraction methods [5]. Taking into account these previous results, it seemed interesting to investigate the Re tetramethylthiourea complex, $[ReO(Me_4tu)_4](PF_6)_3$, as a starting material to other Re(V) complexes by ligand substitution.

As part of the systematic study of this complex, and to learn more about Re coordination chemistry in solution with thiourea derivatives, the present work examines its structure in solution by ^1H and ^{13}C NMR to compare with the reported solid state structure. Its electrochemical behavior is also analyzed by means of cyclic voltamperometric measurements.

$[Re^VOX_4]^-$, $[Re^VOCl_3(PPh_3)_2]$, $[Re^VO(OEt)Cl_2(PPh_3)_2]$ and $[Re^VO_2(PPh_3)_2I]$, where PPh_3 is triphenylphosphine, have been widely used as starting materials for the synthesis of Re(V) monooxo- and dioxocomplexes, by complete or partial ligand substitution [6–12]. The use of the Re(V) cation, $[ReO(Me_4tu)_4]^{3+}$, for preparation of other Re(V) species is described in this article. Diethyldithiocarbamate (Et_2dtc), ethylenediamine (en) and pyridine (py) were selected as test ligands for $[ReO(Me_4tu)_4]^{3+}$. Diethyldithiocarbamate stabilizes Re complexes with the central atom in different oxidation states. In particular, the Re(V) complex $[Re^V_2O_3(Et_2dtc)_4]$ has been previously reported and completely characterized and its structure elucidated by X-ray diffraction methods [13–15]. On the other hand, polyamines form stable *trans*-dioxo hexacoordinate Re(V) complexes, $[ReO_2(amine)_n]^+$, whose properties and structures are well known. $[ReO_2(en)_2]X$ ($X = Cl^-$, I^-, PF_6^-, etc.) is the simplest complex of this series. It has been prepared by several synthetic routes and its structure has also been elucidated by X-ray diffraction [7,9,16–18]. Moreover, $[ReO_2(py)_4]^+$ has been previously synthesized and well characterized [7].

EXPERIMENTAL

Materials

All common laboratory chemicals were purchased from commercial sources and used without further purification.

Characterization

C, H, N and S analyses were performed with a Carlo Erba Model EA1108 elemental analyzer. FTIR spectra (4000–400 cm^{-1}) were measured as KBr pellets on a Bomen M102 instrument. Electronic absorption spectra were performed on a Spectronic 3000 spectrophotometer. Mass spectra were measured on a Shimadzu GC-MS QP 1100EX instrument, at 70 eV. Unit cell parameters and crystalline system of $[Re^V_2O_3(Et_2dtc)_4]$ were determined at room temperature on a Rigaku AFC7S four-circle diffractometer.

Synthesis of $[ReO(Me_4tu)_4](PF_6)_3$

The complex was prepared by reduction of NH_4ReO_4 with stannous chloride in strongly acidic medium, in the presence of excess tetramethylthiourea, according to literature procedure [5]. It was recrystallized and characterized as previously described [5].

^{1}H and ^{13}C Nuclear Magnetic Resonance Experiments

^{1}H NMR and ^{13}C NMR spectra of Me_4tu and $[ReO(Me_4tu)_4]^{3+}$ were recorded at 30°C in deuterated acetonitrile on a Bruker DPX-400 instrument (at 400 and 100 MHz, respectively), with tetramethylsilane as the internal reference. The chemical shifts are reported in ppm.

Heteronuclear correlation experiments (HETCOR), HMQC (multiple quantum) and HMBC (multiple bond), were performed with the same instrument.

Additionally, the effect of temperature on the ^{1}H NMR spectrum of the complex was studied between -40 and $+30$°C.

Electrochemical Measurements

Cyclic voltammetric experiments were performed with a computer controlled PAR (Princeton Applied Research) Potentiostat/Galvanostat model 263A. A standard three-electrode cell was used with a Pt working electrode and a Pt counterelectrode. The Ag reference electrode containing an internal acetonitrile solution 0.01 M in $AgNO_3$ and 0.1 M in tetrabutylammonium hexafluorophosphate ($TBAPF_6$), was incorporated to the cell, with a salt bridge containing 0.1 M $TBAPF_6$ in CH_3CN. The potential of this electrode was calibrated *vs.* NHE using the $[Fe(C_5H_5)_2]^+$/$[Fe(C_5H_5)_2]$ redox couple as an internal standard, for which a potential of $+0.4$ V was assumed [19,20]. Potential values in the text and in the figures are reported in V *vs.* NHE. All the experiments were performed in high purity CH_3CN solutions (Baker, HPLC grade) with 0.1 M $TBAPF_6$ as supporting electrolyte. The concentration of the complex $[ReO(Me_4tu)_4]^{3+}$ was 1 mM. The solvent was dried over 4 Å molecular sieves (Merck) and used without further purification. The supporting electrolyte (electrochemical grade) was purchased from Fluka and used as received. Initial cyclic voltammograms (CVs) were recorded at different scan rates (v) and at 25°C. Prior to each experiment a cyclic voltammogram of the solution containing only the supporting electrolyte was measured. Oxygen was removed by purging the solutions with pure nitrogen and during the measurements a continuous gas stream was passed over the solutions.

Ligand Substitution Studies

Synthesis of $[Re_2O_3(Et_2dtc)_4]$

Sodium diethyldithiocarbamate trihydrate, $NaS_2CNEt_2 \cdot 3H_2O$, (160 mg, 0.710 mmol) was dissolved in acetone (5 mL). This solution was added to recrystallized $[ReO(Me_4tu)_4](PF_6)_3$ (40 mg, 0.035 mmol), previously ground. The color of the solution turned immediately to reddish brown. The solution was stirred for an hour to assure complete substitution. Slow evaporation of the solution at room temperature led to black crystals of $[Re^V_2O_3(Et_2dtc)_4]$, suitable for X-ray diffraction characterization. Crystals were washed, first with methanol (6 × 2 mL) and then with water (3 × 2 mL), to eliminate excess ligand and tetramethylthiourea. Yield = 70%. The identity of the complex was confirmed by elemental analysis, infrared and mass spectra and X-ray diffraction. This material has the same physical properties as the $[Re^V_2O_3(Et_2dtc)_4]$ species prepared by other synthetic routes [6,13,15,21]. Unit cell parameters and space group of the crystals agree with those reported for $[Re^V_2O_3(Et_2dtc)_4]$ [13,21].

Mass spectrum shows the expected fragmentation peaks: $m/z = 499$ (11.30%, $[ReO(Et_2dtc)_2]^+$) and $m/z = 483$ (15.51%, $[Re(Et_2dtc)_2]^+$). The molecular ion was not detected. Peaks show the characteristic pattern of fragments containing Re (Re-187 and Re-185).

Synthesis of $[Re^VO_2(py)_4](PF_6)$

Pyridine (3 mL, 37.2 mmol) was dissolved in acetone (20 mL). This solution was added to $[ReO(Me_4tu)_4](PF_6)_3$ (68 mg, 0.0591 mmol), previously recrystallized and ground. The solution turned reddish yellow immediately. After stirring 30 min to assure complete substitution, an aqueous solution (10 mL) of $NaPF_6$ (250 mg, 1.49 mmol) was added. The reaction mixture was allowed to evaporate slowly at room temperature. Orange crystals of the product were isolated by centrifugation, washed with cold water (3 × 2 mL) and dried *in vacuo*. Yield = 75%. The identity of the complex was confirmed by elemental analysis and by comparison of its infrared and electronic spectra with those previously reported for $[Re^VO_2(py)_4]^+$ [7].

Synthesis of $[Re^VO_2(en)_2](PF_6)$

Synthesis was performed similarly to $[Re^VO_2(py)_4](PF_6)$, starting from ethylenediamine (1 mL, 15.0 mmol) and $[ReO(Me_4tu)_4](PF_6)_3$ (140 mg, 0.120 mmol) in acetone. Yield = 60%. The identity of the complex was confirmed by elemental analysis and by comparison of its infrared and electronic spectra with those reported for $[Re^VO_2(en)_2]^+$ obtained by other synthetic routes [7,9,16].

RESULTS AND DISCUSSION

Nuclear Magnetic Resonance Studies

The NMR experiments show narrow signals, typical for a diamagnetic complex. This was expected since, with few exceptions, Re(V) complexes have been found to be essentially diamagnetic, *i.e.* to contain a spin-paired d^2 configuration [6]. The ^1H and ^{13}C NMR chemical shift values of free Me_4tu and of $[ReO(Me_4tu)_4]^{3+}$ in deuterated acetonitrile at 30°C are listed in Table I.

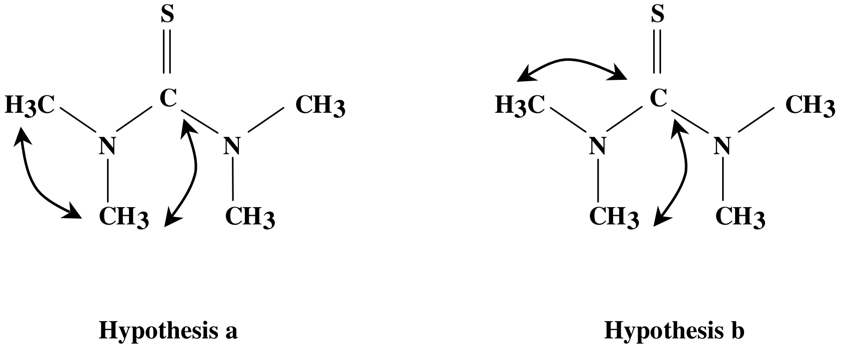
HMQC experiments showed that the proton at δ 3.36 ppm is bonded to the C at δ 44.3 ppm and that the H at δ 3.28 ppm is bonded with the C at δ 44.9 ppm.

The free ligand in solution shows only one ^1H NMR signal, owing to the magnetic equivalence of the four methyl groups emerging from their free rotation around the

TABLE I ^1H and ^{13}C NMR chemical shift values (δ) in ppm of Me_4tu and $[ReO(Me_4tu)_4]^{3+}$ in deuterated acetonitrile at 30°C

		Me_4tu	$[ReO(Me_4tu)_4](PF_6)_3$
^1H NMR	$-CH_3$	3.02	3.28 3.36
^{13}C NMR	$-CH_3$	42.9	44.3 44.9
	$>C{=}S$	194.6	181.0

C–N bond. When the ligand is coordinated, the deshielding effect of the ReO^{3+} *core* (Lewis acid) is apparent at the methyl protons, causing a shift of the ^1H NMR peaks. A similar effect of the ReO^{3+} group has been described for other rhenium monooxo complexes [22,23]. Thus, the signal shifts downfield but also splits into two signals with close chemical shifts (3.28 and 3.36 ppm). Both signals show identical integration, indicating two different kinds of methyl groups in the coordinated Me_4tu. Both are affected differently by the magnetic anisotropy induced by the rhenium atom. So, the complex shows two sets of eight methyl groups magnetically equivalent. Trying to assign these two sets of methyl groups, we took into account the previously reported structure of the complex in the solid state [5]. The coordination polyhedron of the complex is a square pyramid with the substituted thiourea sulfur atoms in the basal positions and the oxo ion located in the summit. The Re atom lies above the plane formed by the sulfur atoms. The base is a perfect square and the Re and O atoms are on the four-fold axis. One dimethylamine group of each ligand molecule remains above the plane formed by the four sulfur atoms and the other lies below it. The SCN_2 group is almost planar, but the planes determined by the N and methyl C atoms are twisted 54.9(6)° relative to each other due to steric hindrance. After complexation through the sulfur atom, a lengthening of the S–C bond and a shortening of both C–N distances with respect to the free ligand is observed owing to increased π character of the C–N bonds. According to the described structure, we would expect four ^1H NMR signals, corresponding to four methyl groups with different chemical and magnetic environments for each Me_4tu. The observation of only two signals could be explained by considering two different hypotheses: (a) both methyl groups bonded to a given nitrogen of Me_4tu are not magnetically equivalent. Moreover, each of them is not distinguishable from one of the methyl groups bonded to the other nitrogen of this Me_4tu ligand; (b) both methyl groups bonded to the same nitrogen are magnetically equivalent but not equivalent to the methyl groups bonded to the other nitrogen of Me_4tu.



SCHEME 1 Schematic representation of hypotheses (a) and (b).

HETCOR experiments differentiated the two possibilities. HMBC experiments showed correlation of the methyl protons exclusively with the thiocarbonyl carbon (δ 181ppm), in agreement with the hypothesis **b** (See Scheme 1). So, one set of magnetically equivalent hydrogens corresponds to the eight methyl groups located over the base of the square pyramid and the other one corresponds to the eight methyl groups located below it. Hypothesis **b** implies the free rotation in solution of the dimethylamine group around the thiocarbonyl carbon–nitrogen bond. The veracity of this assumption was demonstrated by means of ^{1}H NMR experiments performed at low temperatures.

The changes in the ^{13}C NMR spectrum of the ligand after coordination agree with those observed in the ^{1}H NMR experiments. The signals of the methyl carbons are not much displaced, because they are more distant from the Re center. The most distinguishing feature of the ^{13}C NMR spectrum after coordination is the change in the chemical shift of the thiocarbonyl carbon, owing to the effect of the ReO^{3+} *core*. The significant upfield shift stems from the fact that, upon coordination to Re, the electron density on this carbon increases.

These NMR results suggest that the complex ion shows a similar structure in solution and in the solid state.

Variable Temperature Experiments

The results of the HETCOR experiments indicate the magnetic equivalence of both methyl groups bonded to each nitrogen of the ligand molecule, resulting from the free rotation of the dimethylamine group around the thiocarbonyl carbon–nitrogen bond. This free rotation was not expected since the IR and X-ray diffraction studies of the complex, performed in the solid state, demonstrated an increase of the π character of the thiocarbonyl carbon–nitrogen bond upon coordination [5].

^{1}H NMR experiments performed at different temperatures in the range between -40 and $+30$°C showed that a decrease of the temperature produces splitting of both signals detected at 30°C. At -38°C, four signals of similar integration and chemical shifts 3.35, 3.30, 3.22 and 3.14 ppm, corresponding to four magnetically nonequivalent methyl groups of each Me_4tu, are observed. So, in solution at temperatures corresponding to an energy below the rotation energy barrier, free rotation of the dimethylamine group around the thiocarbonyl carbon–nitrogen bond is restricted. Under these experimental conditions (low temperatures), the dissolved complex adopts a rigid structure as observed in the solid state. Above 0–5°C free rotation is allowed and only two signals are detected in the ^{1}H NMR experiments (Fig. 1).

Substitution Studies

$[Re^{V}O_2(en)_2]X$ salts, with $X = I^-$, Cl^- or PF_6^-, have been previously synthesized by ligand substitution onto $[Re^{V}O_2(PPh_3)_2I]$ or substitution/oxidation onto $[Re^{IV}Cl_6]^{2-}$. Also $[Re^{V}O_2(py)_4]X$ salts were prepared by similar methods. Substitution in $[Re^{V}O_2(PPh_3)_2I]$, performed in neat pyridine under heating, leads to $[Re^{V}O_2(py)_4]I$ in high yield. The synthesis using $[Re^{IV}Cl_6]^{2-}$ as starting material needs more energetic conditions, leading slowly to moderate yields (around 40–50%) [7]. $[Re_2^{V}O_3(Et_2dtc)_4]$ has been prepared by refluxing $[ReOCl_3(PPh_3)_2]$ with sodium diethyldithiocarbamate in acetone [14].

In this work, the already known complexes $[Re^{V}O_2(en)_2](PF_6)$, $[Re^{V}O_2(py)_4](PF_6)$ and $[Re_2^{V}O_3(Et_2dtc)_4]$ were successfully prepared by tetramethylthiourea substitution onto $[Re^{V}O(Me_4tu)_4](PF_6)_3$. The substitution of the tetramethylthiourea ligands from the Re coordination sphere of $[ReO(Me_4tu)_4]^{3+}$ by the incoming ligands

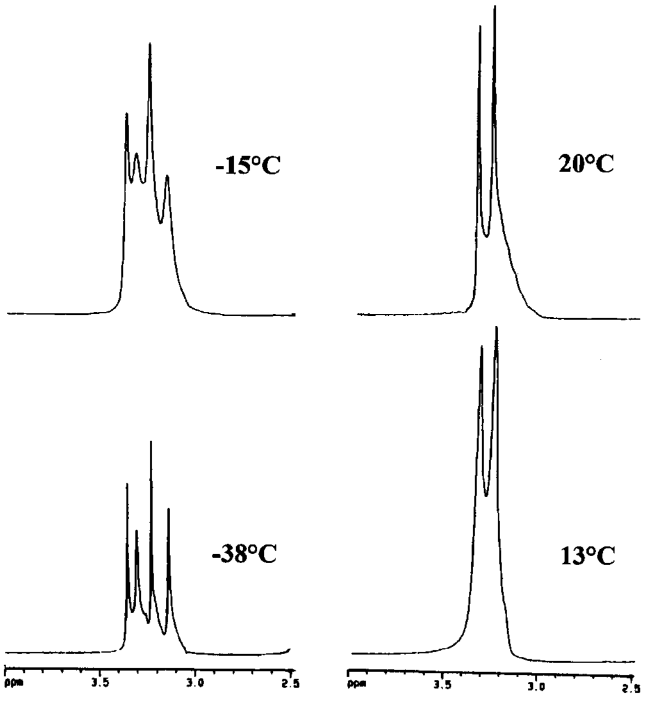


FIGURE 1 ^{1}H NMR experiments performed at different temperatures with the complex $[Re^VO(Me_4tu)_4](PF_6)_3$ in deuterated acetonitrile, showing the chemical shift range of interest.

(Et_2dtc, py or en) occurs quickly and under mild conditions. The yield of substituted complex is high in all cases.

The complex $[ReO(Me_4tu)_4](PF_6)_3$ seems, therefore, to be a suitable starting material for the synthesis of other Re(V) complexes by ligand substitution. In the reported experiments, the preparation of Re(V) complexes with the *cores* *trans*-ReO_2^+ and $Re_2O_3^{4+}$ was illustrated. Obviously, which Re(V) *core*, *trans*-ReO_2^+, ReO^{3+} or $Re_2O_3^{4+}$, is stabilized, depends on steric and/or electronic aspects of the incoming ligand. In the selected experimental conditions no Me_4tu remains coordinated. Depending on the incoming ligand nature and on the selected experimental conditions, the other Re(V) precursors previously mentioned can lead to mixed ligand complexes by partial ligand substitution. Having a single type of ligand in its coordination sphere and tetramethylthiourea as a labile ligand, $[ReO(Me_4tu)_4]^{3+}$ avoids the formation of mixed ligand coordination compounds. Obviously, the formula of the substituted complex is determined not only by the precursor and the experimental conditions but also by the incoming ligand. These results are encouraging to make further attempts to synthesize, by ligand substitution onto $[Re^VO(Me_4tu)_4]^{3+}$, other Re(V) complexes with different incoming ligands.

Electrochemistry

The redox behavior of $[ReO(Me_4tu)_4]^{3+}$ was investigated using cyclic voltammetry. CVs of a 10^{-3} M solution in CH_3CN were recorded at different scan rates (v), between 1.35 and −0.9 V as potential limits, and the results will be briefly discussed.

Figure 2(a and b) contains selected voltammograms showing the observed features, as a function of increasing scan rates, at 25°C.

As the potential is scanned in a negative direction, at all scan rates investigated (0.02–15 V/s), only one reduction peak (A) is observed on the first scan. Upon reversing the potential at −0.9 V and scanning in the positive direction, different oxidation

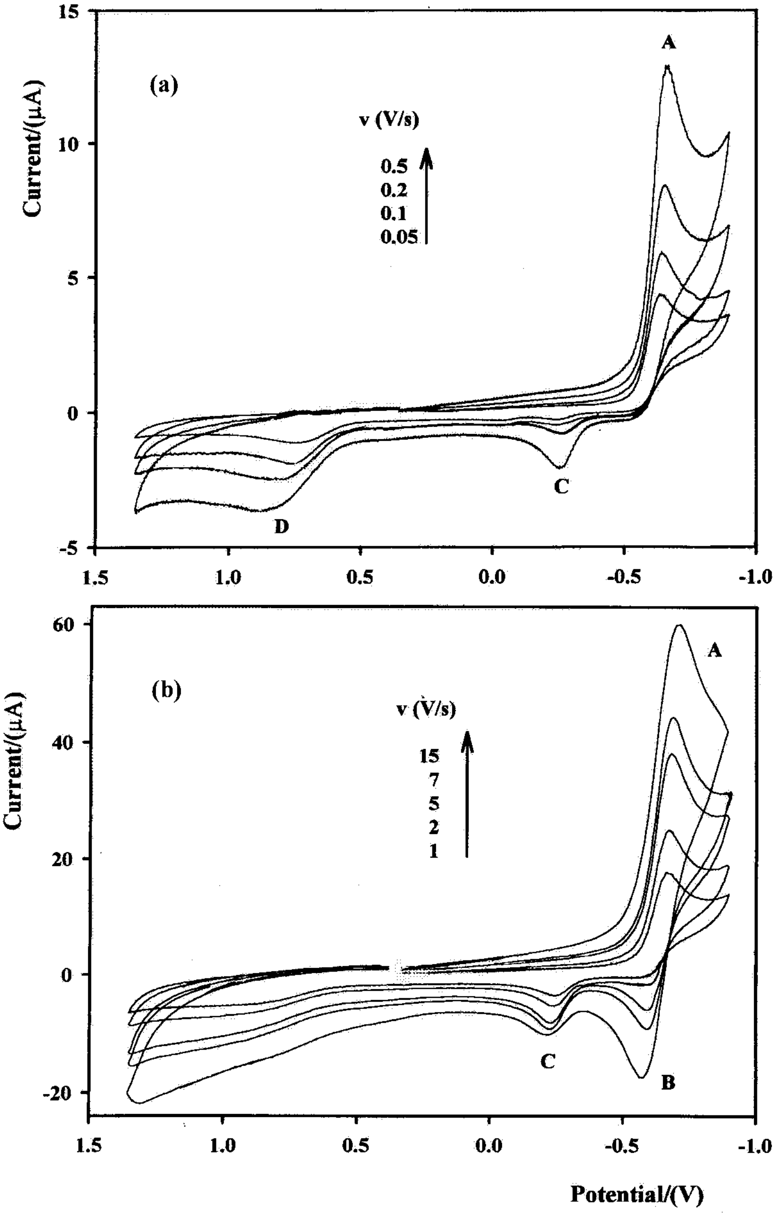


FIGURE 2 Selected cyclic voltammograms (CVs) at 25°C of 10^{-3} M $[ReO(Me_4tu)_4]^{3+}$ in CH_3CN/0.1 M $(TBA)PF_6$. Experimental conditions described in the text. (a): CVs obtained at $v \leq 0.5$ V/s, (b): CVs recorded at $v \geq 1$ V/s.

processes, which are strongly scan rate dependent, are evident. At $v \leq 1$ V/s only a slight residual anodic wave (B), corresponding to the foregoing reduction process, is observed. As the scan continues in the positive direction, two oxidation contributions, with a clearly defined peak C and a wave D, appear. At $v = 2$ V/s, the oxidation peak B starts to develop and its current contribution grows at increasing v values. Simultaneously, wave D broadens and finally disappears. Moreover, at $v \geq 10$ V/s, the current associated with peak C, when measured from decaying baseline of peak B, diminishes. On the second scan a new small wave, that can be associated with peak C, appears (data not shown). The lack of the anodic process B, at slow v, and the presence of both contributions (C, D) only after the first cathodic scan indicate that a coupled chemical reaction takes place after the initial reduction of the title compound.

Therefore, for diagnostic purposes, and taking into account that it was difficult to define proper baselines for the anodic peak B, the variation of the ipa(B)/ipc(A) ratio as a function of the scan rate was determined using an empirical relation derived by Nicholson [24,25]. Also, the currents of each CV were normalized for changes in the scan rates ($i/v^{1/2}$). When plotted in this way all curves are shown on the same relative scale, and direct comparison can be done (Fig. 3). From analysis of the experimental results, the following trends are observed:

(1) The anodic to cathodic peak current ratio, ipa(B)/ipc(A), is less than one, but approaches a value of unity at higher scan rates. This ratio increases from 0.53 to 0.83 when the scan rate increases from 0.1 to 15 V/s.

(2) The cathodic peak potential, Epc, shifts slightly to more negative potentials on increasing v values.

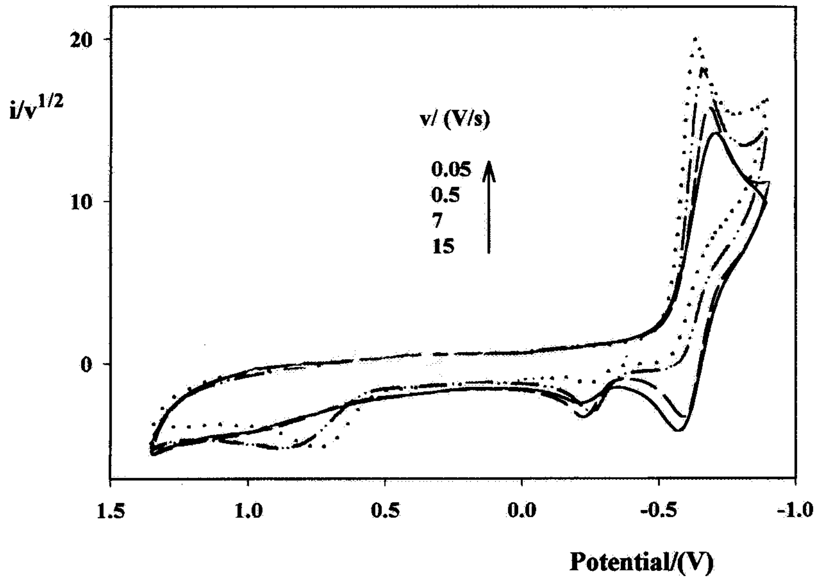


FIGURE 3 Comparative cyclic voltammograms of the complex at selected scan rates plotted with the currents normalized for changes in v ($i/v^{1/2}$). Note that at the higher scan rate the current function, ipc(A)/$v^{1/2}$, is lower than at the slower scan rates.

(3) The plot of the peak current associated with the reduction process A, as a function of $v^{1/2}$ is not linear in the range of scan rates investigated, indicating that two non-equivalent processes are involved.

(4) The plot of ipc(A)/$v^{1/2}$ as a function of v shows that this ratio is much higher at low than at high v values. This ratio diminishes from 20.8 to 13.7 μA $s^{1/2}V^{-1/2}$ when the scan rate increases from 0.02 to 15 V/s (Fig. 4).

These trends suggest that the redox behavior of this compound can be explained through an $E_rC_iE_r$ mechanism (a chemical reaction coupled between two electron-transfer reactions), which can be summarized, in a general way, as follows:

$$O_1 + n_1e^- \rightleftharpoons R_1 \qquad E_1^o \tag{1}$$

$$R_1 \xrightarrow{k_1} O_2 \tag{2}$$

$$O_2 + n_2e^- \rightleftharpoons R_2 \qquad E_2^o \tag{3}$$

This process has been treated intensively by Nicholson and Shain for both linear and cyclic voltammetry [26,27]. On the basis of this theoretical work, the changes observed in the cyclic voltammograms as a consequence of the different scan rates indicate that, in the present case, the potential necessary for the second reduction is less negative than that required for the first reduction. Hence, the reduction of the species O_2 is thermodynamically more favorable than that of O_1.

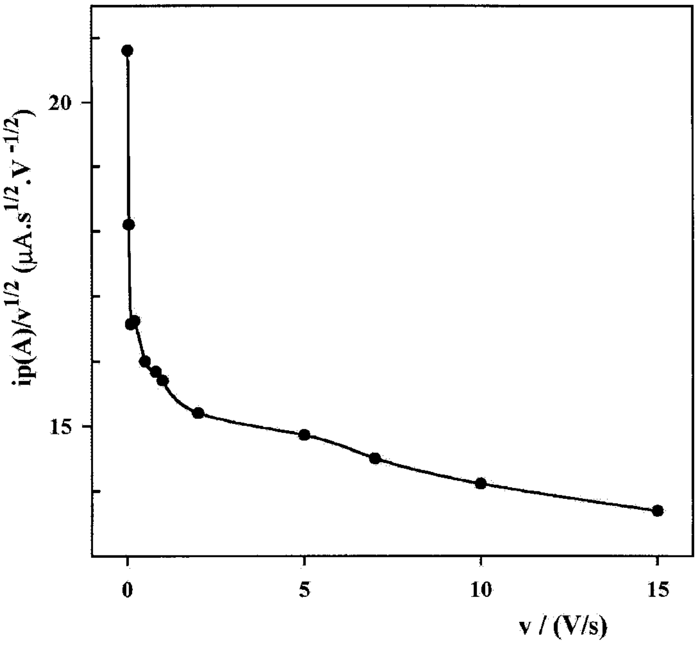


FIGURE 4 Variation of ipc(A)/$v^{1/2}$ with changes in scan rate.

It is clear from the above scheme that if the measurements are carried out in a sufficiently short time (fast v) reaction (2) will not have time to proceed. In this case the electrochemical response will have the appearance of an unperturbed n_1 electron reversible process. In the other extreme, if v is slow, the chemical reaction will go to completion and the cathodic response will have the appearance of an $n_1 + n_2$ electron process. In the intermediate case the response must lie between these extremes, and changes on the cyclic voltammogram must be also observed on the reverse and subsequent scans [25].

We can now explain the voltammetric behavior and assign the peaks to actual reactions of the cation $[ReO(Me_4tu)_4]^{3+}$.

On the first cathodic scan only the reduction of the metal center from Re(V) to Re(IV) or even Re(III) is produced. This step is strongly time dependent.

Peak A, in Fig. 2, is due to the initial one-electron reduction of the original compound from Re(V) to Re(IV) followed by a chemical reaction to form a new electroactive species Re(IV)*. This product is more easily reduced than the starting molecule and undergoes further reduction at the applied potential. This reaction is accompanied by the loss of ligand molecules from the coordination sphere.

At high scan rates, the effect of the follow-up chemical reaction is minimized (the ipa/ipc ratio tends to one) and the over-all reaction tends toward that of a simple one-electron reduction. Peak B corresponds to the reverse reaction, oxidation of the original Re(IV)–Re(V).

However on increasing the time-scale of the experiment by decreasing v, the instability of the reduced complex is evident. In this case, a chemical step has a significant effect before the potential value is suitable to oxidize back the Re(IV) and the above mentioned new intermediate species Re(IV)* is formed. The reduction of this species from Re(IV)* to Re(III)* mainly contributes to the total reduction current of peak A and there is a trend toward a two-electron reduction process ($ipc/v^{1/2}$ is higher at small v). Thus, on the reverse scan the current associated with the peak B is smaller than that obtained at faster scan rates.

In addition, both anodic peaks C and D, that appear only after the first cathodic scan, are the result of the oxidation of the Re(III)* species and ligand molecules, respectively. This last fact was confirmed with an independent measurement performed with the ligand in similar experimental conditions. The presence and behavior of this peak supports the idea that the instability of the reduced original compound is directly associated with the loss of ligand from the coordination sphere.

Reactions occur according to the following $E_rC_iE_r$ electrode mechanism:

$$[Re^{V}OL_4]^{3+} + e^- \rightleftharpoons [Re^{IV}OL_4]^{2+} \qquad E_1^o \qquad (1)$$

$$[Re^{IV}OL_4]^{2+} \longrightarrow [Re^{IV*}OL_{(4-x)}]^{2+} + xL \qquad (2)$$

$$[Re^{IV*}OL_{(4-x)}]^{2+} + e^- \rightleftharpoons Re^{III*} - L \text{ (unknown species)} \qquad E_2^o \qquad (3)$$

The unstable Re(IV) species was not identified, but previous voltammetry experiments lend support to the existence of oxorhenium(IV) complexes resulting from the addition of one electron to Re(V) oxospecies without any marked geometric change. Moreover, the decay of the Re(IV) intermediate complex has been presumed to involve ligand dissociation [18,28].

Furthermore, the very weak signal obtained for peak C, at low *v*, and its counterpart on the second scan could indicate that the ECE scheme described above is disturbed by a further follow-up chemical reaction ($E_rC_iE_rC_i$ mechanism). It is known that in many processes, the product of the second charge transfer (reaction (3)) may also be unstable and it can eventually disappear by a following reaction. In this case, the corresponding waves will be absent, but the initial peak and its counterpart (A–B pair in our case) will show behavior near that of $E_rC_iE_r$ [25].

Thus, despite the instability of the Re(III)* species correlations between experiment and theory and the behavior of the A–B couple at different scan rates allow the redox mechanism for the title compound to be proposed.

Acknowledgments

The authors gratefully acknowledge financial support from Programa para el Desarrollo de las Ciencias Básicas (PNUD – UNESCO), Third World Academy of Sciences, Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina and Agencia Nacional de Promoción Científica y Tecnológica, Argentina (PICT-06148). BSPC and EJB are members of the Research Career from CONICET. We also wish to thank Prof. G. Seoane for fruitful discussions on NMR results.

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