PERGAMON

Polyhedron 18 (1999) 2099–2107

POLYHEDRON

New Re(III) complexes with alkylthioureas as precursors to other Re(III) compounds. Crystal structures of $[Re(N\text{-ethylthiourea})_6](PF_6)_3$ and $[Re(N,N'\text{-dimethylthiourea})_6](PF_6)_3$

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Received 1 September 1998; accepted 31 March 1999

Abstract

New Re(III) complexes with thiourea derivatives have been synthesized by reduction of perrhenate with tin(II) chloride in 2N hydrochloric acid in the presence of excess alkylthiourea. The obtained compounds were $[Re^{III}(\text{alkylthiourea-S})_6]X_3.nH_2O$, where X is Cl^- or PF_6^- and alkylthiourea is *N*-methylthiourea (Metu), N,N′-dimethylthiourea (Me_2tu) or *N*-ethylthiourea (Ettu). Complexes were characterized by elemental and thermal analyses and by electronic and FTIR spectroscopy. Their kinetic stabilities in aqueous and methanolic solutions were also studied. Results were compared with those previously reported for $[Re^{III}(tu\text{-}S)_6]Cl_3.4H_2O$, where tu=thiourea. Molecular structures of $[Re^{III}(Ettu)_6](PF_6)_3$ and $[Re^{III}(Me_2tu)_6](PF_6)_3$ were determined by single crystal X-ray diffraction methods. The coordination polyhedra around the Re(III) ion are distorted octahedra. The six alkylthiourea ligands are sulfur bonded to the central atom [*d*(Re–S) ranges from 2.402(4) to 2.441(4) Å for the ethylthiourea complex and from 2.416(3) to 2.446(3) for the dimethylthiourea one]. Capability of working as starting materials via ligand substitution, in methanolic medium for these new Re(III) complexes and for previously reported $[Re^{III}(tu)_6]Cl_3.4H_2O$ is stated. Selected incoming ligands, 1,2-bis(diphenylphosphino) ethane (dppe) and 1,3-bis(diphenylphosphino) propane (dppp), lead to the already known $[Re^{III}(dppe)_2Cl_2]Cl.2MeOH$ and $[Re^{III}(dppp)_2Cl_2]Cl$ with good yields. Re(III) complexes with thiourea and alkylthioureas can be ordered according to their substitution rate as follows: $[Re(tu)_6]^{3+} < [Re(Ettu)_6]^{3+} \cong [Re(Metu)_6]^{3+} < [Re(Me_2tu)_6]^{3+}$. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Rhenium(III); Alkylthioureas complexes; $[Re(N\text{-ethylthiourea})_6](PF_6)_3$ structure; $[Re(N,N'\text{-dimethylthiourea})_6](PF_6)_3$ structure; Ligand substitution onto Re(III)-alkylthioureas; Synthesis of diphosphine rhenium(III) complexes by ligand substitution

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1. Introduction

Owing to the extensive use of the γ-emitter ^{99m}Tc in diagnostic nuclear medicine and the potential usefulness of ^{186}Re and ^{188}Re for radiotherapeutic purposes, the chemistry of Tc and Re compounds has become an active field of research [1–4].

Ligand substitution onto suitable precursors is an important route of synthesis of Tc complexes. Being thiourea (tu) a poor ligand, its easy substitution under mild conditions turned $[Tc^{III}(tu\text{-}S)_6]Cl_3$ into a useful precursor to other Tc(III) compounds in aqueous and methanolic media [5–10]. *N*-methylthiourea (Metu) and *N,N′*-dimethylthiourea (Me_2tu) are also able to stabilize Tc(III). $[Tc^{III}(Metu\text{-}S)_6]^{3+}$ and $[Tc^{III}(Me_2tu\text{-}S)_6]^{3+}$ complexes have been prepared and characterized [11,12]. These Tc complexes have also been tested as precursors for further Tc(III) compounds [13,14].

Ligand substitution onto suitable precursors is also an important route of synthesis of Re complexes. This synthetic route relies on labile Re species as preparative intermediates [15–20]. Syntheses of Re(III) complexes described in the literature are mainly based on substitution onto the *trans*-$[ReCl_3(NCCH_3)(PPh_3)_2]$ precursor, which usually leads to mixed-ligand neutral species. Only scarce examples of complete ligand substitution onto this precursor are reported [21]. Moreover, this precursor is not suitable for ligand substitution in aqueous media. So, substitution reactions are commonly performed in organic

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0277-5387/99/$ – see front matter
PII: S0277-5387(99)00096-0

solvents such as dichloromethane, benzene or acetonitrile [15,16,22–24].

On the other hand $[Re^{III}(thiourea\text{-}S)_6]Cl_3.4H_2O$ has recently been synthesized and fully characterized [25]. Taking into account the chemical analogy between Re and Tc compounds, this complex is obviously a potential precursor to other Re(III) compounds, by ligand substitution. Alkylthioureas are also expected to stabilize Re(III) by sulfur bonding to central atom. These $[Re^{III}(alkylthiourea\text{-}S)_6]^{3+}$ compounds could be also tested as precursors. Differences in reactivity of these compounds are expected, mainly due to the presence of bulkier groups (compared to hydrogen) bonded to thioureas nitrogens surrounding the central Re(III) atom. As in Tc(III) compounds, substitution is expected to proceed via a dissociative intimate mechanism [26]. Therefore, changes in leaving ligand nature can be a suitable way to modify substitution kinetics, and provide a wider range of precursors which could find much use in the synthesis of other Re(III) complexes in aqueous or alcoholic media.

We report here results on synthesis and full characterization of $[Re^{III}(alkylthiourea)_6]X_3.nH_2O$ complexes, where X is Cl^- or PF_6^- and alkylthiourea is *N*-methylthiourea, N,N′-dimethylthiourea or *N*-ethylthiourea (Ettu). Molecular structures of $[Re^{III}(Me_2tu)_6](PF_6)_3$ and $[Re^{III}(Ettu)_6](PF_6)_3$ were determined by single crystal X-ray diffraction methods and they are reported here.

A comparative stability study in aqueous and methanolic media with the $[Re^{III}(thiourea)_6]Cl_3$ complex previously reported, has also been performed for all new compounds. Capability of working as starting materials via ligand substitution in methanolic medium, is stated for $[Re^{III}(thiourea)_6]Cl_3$ and alkylthioureas Re(III) complexes with 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis-(diphenylphosphino)propane (dppp) as incoming ligands.

2. Experimental

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

2.1. Preparation of hexakis(alkylthiourea-S) rhenium(III) tri(hexafluorophosphate) compounds (alkylthiourea=N-methylthiourea, N,N′-dimethylthiourea or N-ethylthiourea)

$SnCl_2.2H_2O$ (200 mg, 0.89 mmol) was dissolved in 2N HCl (5.5 cm^3). A mixture of alkylthiourea (15 mmol) and NH_4ReO_4 (100 mg, 0.37 mmol) was added to the solution. The solution was stirred overnight at room temperature and filtered off, if necessary. After keeping the final solution at −5°C for 1 h, 0.5ml of a 6M $NaPF_6$ aqueous solution was added. The yellowish solids obtained were washed with small portions of cold water, and dried. The compounds are soluble in acetone, acetonitrile and methanol, slightly soluble in ethanol and insoluble in water. Thermal analyses TGA and DTA of $[Re(Metu)_6](PF_6)_3$ agreed with one water molecule of crystallization per complex ion (1.4% weight loss centered at 120°C, 1.5% calc.). Absence of water molecules of crystallization was demonstrated for Me_2tu and Ettu complexes.

2.1.1. $[Re^{III}(N\text{-methylthiourea-}S)_6](PF_6)_3 \cdot H_2O$

Yield 60%. The complex was recrystallized from an ethanolic solution by slow evaporation at room temperature. Anal (%): Found: C, 12.5; H, 3.1; N, 14.1; S, 16.4; Re, 15.3. Calc. for $C_{12}H_{36}N_{12}S_6Re\ P_3F_{18} \cdot H_2O$: C, 12.2; H, 3.2; N, 14.2; S, 16.3; Re, 15.8. Electronic spectrum (ethanol): 358sh, 387 ($8.1 \times 10^3\ M^{-1}cm^{-1}$), 410 sh, 454 ($4.8 \times 10^3\ M^{-1}cm^{-1}$), 241 nm.

2.1.2. $[Re^{III}(N,N'\text{-dimethylthiourea-}S)_6](PF_6)_3$

Yield 30%. The complex was recrystallized by slow evaporation at room temperature of a 1:1 (v/v) mixture acetone/2N HCl (0.04M Me_2tu). Single deep red crystals, suitable for X-ray analysis were obtained by this procedure. Anal. (%): Found: C, 17.4; H, 3.5; N, 13.2; S, 15.0; Re, 15.2. Calc. for $C_{18}H_{48}N_{12}S_6Re\ P_3F_{18}$: C, 17.3; H, 3.9; N, 13.5; S, 15.4; Re, 14.9. Electronic spectrum (acetone): 370 sh, 391 ($6.0 \times 10^3\ M^{-1}cm^{-1}$), 425sh, 471 ($3.5 \times 10^3\ M^{-1}cm^{-1}$) and 239 nm (ethanol).

2.1.3. $[Re^{III}(N\text{-ethylthiourea-}S)_6](PF_6)_3$

Yield 50%. Single deep red crystals, suitable for X-ray analysis were obtained from a methanolic solution by slow evaporation at room temperature. Anal (%): Found: C, 17.6; H, 3.6; N, 13.5; S, 15.0. Calc. for $C_{18}H_{48}N_{12}S_6Re\ P_3F_{18}$: C, 17.3; H, 3.9; N, 13.5; S, 15.4. Electronic spectrum (ethanol): 329sh, 389 ($9.4 \times 10^3\ M^{-1}cm^{-1}$), 417 sh, 469 ($6.4 \times 10^3\ M^{-1}cm^{-1}$), 241 nm.

2.2. Preparation of hexakis(alkylthiourea-S) rhenium(III) trichloride compounds

These salts were obtained from the same solutions previously detailed for the isolation of hexafluorophosphate salts. For all of them, thermal analyses showed no water molecules of crystallization.

2.2.1. $[Re^{III}(N\text{-methylthiourea-}S)_6]Cl_3$

This salt was obtained by adding a high volume of acetone (50 cm^3) to the reaction mixture. A bright yellow solid was isolated and washed with acetone. Yield 64%. The compound was recrystallized from a 2N HCl (0.2M Metu)/acetone solution. Anal. (%): Found: C, 17.2; H, 4.2; N,19.6; S, 22.8; Re, 21.3. Calc. for $C_{12}H_{36}N_{12}S_6\ ReCl_3$: C, 17.3; H, 4.3; N, 20.1; S, 23.0; Re, 22.3. Electronic spectrum (ethanol): 359sh, 385 ($7.2 \times 10^3\ M^{-1}cm^{-1}$), 405 sh, 453 ($4.3 \times 10^3\ M^{-1}cm^{-1}$), 241 nm. The compound is soluble in water, ethanol and methanol and insoluble in acetone.

2.2.2. [Re^{III}(N,N′-dimethylthiourea-S)$_6$]Cl$_3$

This salt was obtained using a reaction mixture volume of 2.7 cm^3. A yellow solid appeared after stirring overnight. It was dissolved in acetone and a white solid, probably excess ligand, was discarded. The acetone solution was evaporated to dryness and the sticky solid was treated with n-butanol to give a yellow solid which was then washed with several small portions of n-buthanol. Yield: 20%. Anal (%): Found: C, 24.1; H, 5.3; N, 17.8; S, 20.5. Calc. for $C_{18}H_{48}N_{12}S_6ReCl_3$: C, 23.6; H, 5.3; N, 18.3; S, 20.9. Electronic spectrum (aqueous 2N HCl): 363 sh, 391 (5.1×10^3 M^{-1} cm^{-1}), 409 sh, 454 (2.1×10^3 M^{-1} cm^{-1}), 240 nm. The compound is soluble in water, acetonitrile and methanol and less soluble in acetone and ethanol.

2.2.3. [Re^{III}(N-ethylthiourea-S)$_6$]Cl$_3$

This compound was also obtained using a lower reaction volume (2.7 cm^3). A dark orange solid was isolated by keeping the solution for several days at −5°C and dried under vacuo. Yield: 50%. Anal (%): Found: C, 23.1; H, 5.3; N, 17.8; S, 20.5. Calc. for $C_{18}H_{48}N_{12}S_6ReCl_3$: C, 23.6; H, 5.3; N, 18.3; S, 20.9. Electronic spectrum (methanol): 328 sh, 387 (9.0×10^3 M^{-1} cm^{-1}), 417 sh, 468 (5.8×10^3 M^{-1} cm^{-1}), 240 nm. The compound is soluble in water and methanol and less soluble in acetone and ethanol.

2.3. Characterization

C, H, N and S elemental analyses were carried out with a Carlo Erba Model EA 1108 elemental analyzer. Rhenium was determined spectrophotometrically by reaction with α-furyldioxime, modifying a reported method [27].

Thermogravimetric and differential thermal analyses (TGA and DTA) were performed up to 400°C on Shimadzu analyzers TGA-50 and DTA-50 (calcined Al_2O_3 as reference) with a 50 cm^3 min^{-1} N_2 flow and a heating rate of 6°C min^{-1}.

FTIR spectra (4000–400 cm^{-1}) were measured as KBr pellets on a Bruker IFS 66 instrument. Low frequencies FTIR spectra (500–50 cm^{-1}) were performed as polyethylene pellets on a Bruker 113v equipment.

Electronic absorption spectra were performed on a Spectronic 3000 spectrophotometer.

Kinetic stability studies were carried out as previously described for $[Re(tu)_6]Cl_3.4H_2O$ [25]. Decomposition of $[Re(Metu)_6]Cl_3$, $[Re(Ettu)_6]Cl_3$ and $[Re(Me_2tu)_6]Cl_3$ in the different conditions tested, i.e. aqueous or methanolic solution 10^{-3}–10^{-4} M, pH range 1–5 and temperature 25.0°C±0.1, was followed spectrophotometrically. For a fixed set of conditions, the remaining percentage of the Re complex at each time was determined as the quotient between measured absorbance and initial absorbance.

2.4. Ligand substitution experiments onto [ReL$_6$]X$_3$ (L= tu, Metu, Ettu or Me$_2$tu; X=Cl$^-$ or PF$_6^-$) by dppe and dppp

0.1 mmol of $[ReL_6]X_3$ were dissolved in a mixture of 15 ml of methanol and 0.2 ml of 12N HCl. To this yellow solution 1,2-bis(diphenylphosphino)ethane (dppe) (200 mg, 0.5 mmol) or 1,3-bis(diphenylphosphino)propane (dppp) (200 mg, 0.48 mmol) was added. The reaction mixture was heated to reflux (6–7 h). Solvent was evaporated in vacuo to about 5 ml. The diphosphine complex was isolated by keeping the solution at 2–8°C for at least 2 days. For dppe, a red intermediate (λ_{max}=474 nm) was detected during the refluxing period which turned completely into the final orange $[Re(dppe)_2Cl_2]^+$ complex.

2.4.1. [Re^{III}(dppp)$_2$Cl$_2$]Cl

The yellow solid was recrystallized from dichloromethane-methanol-2N HCl by slow evaporation at room temperature. Electronic spectrum (methanol): 432 nm. Main IR bands: 3063 (CH stretching of the phenyl groups), 2932 (CH_2 stretching), 1484 (CH_2 bending), 1434 (P–phenyl stretching), 1092 (C–C stretching), 745 and 697 (out of plane CH_2 bending), 327 cm^{-1} (Re–Cl stretching) [28]. The compound is a 1:1 electrolyte in acetonitrile. Anal (%): Found: C, 56,2; H, 5.9. Calc. for $C_{54}H_{52}Cl_2P_4ReCl\cdot H_2O.CH_3OH$: C, 56.6; H, 5.4. Yields and times required to complete ligand substitution were determined and reported in Table 1.

2.4.2. [Re^{III}(dppe)$_2$Cl$_2$]Cl.2MeOH

The orange solid was washed with ether/ethanol (10:1 v/v) and dried in vacuo. Yields: 40–55%. Crystals suitable for X-ray diffraction determinations were obtained by slow evaporation of a methanol solution at room temperature. Anal (%): Found: C, 56.3%; H, 4.4%. Calc. for $C_{52}H_{48}Cl_2P_4ReCl.2CH_3OH$: C, 56.2%; H, 4.9%. Crystal data, together with electronic and IR spectra agreed with those previously reported for $[Re(dppe)_2Cl_2]Cl.2MeOH$ [29,30].

Table 1
Yield and time required for the Re(III) precursors to complete ligand substitution with dppp as incoming ligand

	Yield (%)	Time[a] (h)
$[Re(tu)_6]^{3+}$	55	4.5
$[Re(Metu)_6]^{3+}$	70	1.0
$[Re(Ettu)_6]^{3+}$	75	1.2
$[Re(Me_2tu)_6]^{3+}$	58	0.5

[a] Time necessary to complete substitution of the alkylthiourea or thiourea by dppp.

2.5. X-ray diffraction data and crystal structure determination and refinement of [Re(Ettu)$_6$](PF$_6$)$_3$ and [Re(Me$_2$tu)$_6$](PF$_6$)$_3$

Crystal data, data collection procedure, structure determination methods and refinement results are summarized in Table 2. The observed trend of an increase in the thermal parameters of the ethyl and dimethylthiourea ligands toward their free ends suggests relatively large librational vibrations and/or displacive disorder of these groups. Several hydrogen atoms were located at approximate positions in a difference Fourier map suggesting that amide hydrogens lay on $S{=}CN_2C_{ethyl}$ planes for [Re(Ettu)$_6$](PF$_6$)$_3$ and on $S{=}C(NC_{methyl})_2$ planes for

Table 2
Crystal data and structure solution methods and refinement for [Re(SC(NHCH$_3$)$_2$)$_6$](PF$_6$)$_3$ (**I**) and [Re(SC(NH$_2$)NHCH$_2$CH$_3$)$_6$](PF$_6$)$_3$ (**II**)

	Structure I	Structure II
Empirical formula	$C_{18}H_{48}N_{12}S_6ReF_{18}P_3$	$C_{18}H_{48}N_{12}S_6ReF_{18}P_3$
Formula weight	1246.15	1246.15
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1cn$[f]
Unit cell dimensions	[a]	[g]
a (Å)	13.239(3)	11.828(2)
b (Å)	20.905(6)	15.484(2)
c (Å)	17.005(5)	25.099(3)
β (°)	102.240(2)	
Cell volume (Å^3)	4599(2)	4597(1)
Formula units/unit cell	4	4
D_{calc} (Mg/m^3)	1.800	1.801
Absorption coefficient	3.124 mm^{-1}	3.126 mm^{-1}
F(000)	2472	2472
Crystal size	0.20×0.15×0.07 mm	0.14×0.20×0.32 mm
Crystal color/shape	Red/parallelepiped	Red/parallelepiped
Diffractometer/scan	Enraf-Nonius CAD-4/$\omega-2\theta$	
Radiation, graphite monochromator	MoKα, $\lambda=0.71073$ Å	
Scan width	$0.8+0.35\tan\theta$	
Standard reflection	(−2,8,7)	(1,2,−14)
Decay of standard (%)	±2%	±2%
θ range for data collection	1.57 to 24.99°	1.55 to 27.96°
Index ranges	$-15\le h\le 15$, $0\le k\le 24$, $0\le l\le 20$	$0\le h\le 15$, $0\le k\le 20$, $-1\le l\le 33$
Reflections collected	8633	6308
Independent reflections	6477 [$R_{symm}=0.034$]	4906 [$R_{symm}=0.049$]
Observed reflections [$I>2\sigma(I)$]	3668	3006
Data reduction and correction	[b]	[h]
and structure solution[c] and refinement[d] programs	SDP [39],SHELX-76 [40], SHELX-86 [41], SHELX-93 [42]	
Refinement method	Full-matrix least-squares on F^2	
Weights, *w*	$[\sigma^2(F_o^2)+(0.05P)^2+1.19P]^{-1}$ $P=[\mathrm{Max}(F_o^2,0)+2F_c^2]/3$	$[\sigma^2(F_o^2)+(0.0522P)^2+0.68P]^{-1}$
Data/restraints/parameters	6477/0/524	4906/1/524
Goodness-of-fit on F^2	1.061	1.048
Final *R* indices[e] [$I>2\sigma(I)$]	$R_1=0.058$, $wR_2=0.111$	$R_1=0.0481$, $wR_2=0.0973$
R indices (all data)	$R_1=0.126$, $wR_2=0.138$	$R_1=0.1031$, $wR_2=0.1202$
Absolute structure parameter		−0.006(12)
Largest diff. peak and hole	0.79 and −0.83 e.Å^{-3}	0.913[i] and −1.205 e.Å^{-3}

[a] Least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 22 reflections in the $17.54<2\theta<27.04°$ range.

[b] Corrections: Lorentz, polarization and absorption [38]. The maximum and minimum transmission factors were 0.814 and 0.598.

[c] Neutral scattering factors and anomalous dispersion corrections.

[d] Structure solved by Patterson and Fourier methods and the final molecular model obtained by anisotropic full-matrix least-squares refinement of non-hydrogen atoms.

[e] *R* indices defined as: $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

[f] Related to the standard space group $Pna2_1$ by the interchange of *a* and *c* axes.

[g] Least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 25 reflections in the $23.6<2\theta<34.9°$ range.

[h] Corrections: Lorentz, polarization and absorption [38]. After this later correction, the R_{sym} agreement factor among symmetry related reflections dropped from 0.049 to 0.026; the corresponding maximum and minimum transmission factors were 0.706 and 0.523.

[i] Located close to the rhenium atom position.

$[Re(Me_2tu)_6](PF_6)_3$ and that methyl hydrogens are at staggered positions. All hydrogens were positioned on stereochemical basis and included in the refinement riding on the atom to which they are bonded with a common isotropic thermal parameter, which in the final run converged to $U=0.12(1)$ Å^2 for $[Re(Ettu)_6](PF_6)_3$ and to $U=0.16(1)$ Å^2 for $[Re(Me_2tu)_6](PF_6)_3$.

3. Results and discussion

Reduction of perrhenate by stannous chloride in strongly acidic aqueous solution in presence of excess *N*-methylthiourea or *N*-ethylthiourea leads to the formation of hexafluorophosphate and chloride salts of $[Re(Metu)_6]^{3+}$ and $[Re(Ettu)_6]^{3+}$ with good yields, though the ethylthiourea complex is more difficult to isolate due to the formation of sticky solids. Regarding *N*,*N'*-dimethylthiourea, the yields are lower. The reaction proceeds via a dark red intermediate, that does not disappear completely. Probably a Re(V) oxo dimethylthiourea complex is formed, as reported in the synthesis of $[Re(tu)_6]^{3+}$ [25].

The electronic spectra of all the complexes show a band shape similar to that reported previously for $[Re(tu)_6]Cl_3$. The visible spectra show also a similar pattern to the Tc analogs but shifted to higher frequencies [11,12,25].

The FTIR spectra (4000–400 cm^{-1}) of the six compounds rule out the presence of ReO_2^+, ReO^{3+} or μ-oxo species since the characteristic absorptions of these moieties around 830 cm^{-1} and in the 1000–900 cm^{-1} region are not detected [15,16]. Typical signals of the ligands are found in the complexes [31,32]. Previous theoretical assignment of the IR bands for the free *N*-ethylthiourea ligand was not available. Tentative assignments are made based on those for *N*-methylthiourea. The hexafluorophosphate salts show in addition the ν_{as}(PF) and δ_{as}(FPF) of the PF_6^- moiety [33]. Main bands for $[Re(Metu)_6](PF_6)_3 \cdot H_2O$: 3348 s, 3318 s and 3282 s (NH and symmetric and asymmetric NH_2 stretchings), 2970 vw and 2850 vw (symmetric and asymmetric CH_3 stretchings), 1635 s (NH_2 bending), 1578 s (combination mode of CN and CS stretchings and NCN bending), 1503 s (CN asymmetric stretching), 1461w and 1422 m (symmetric and asymmetric CH_3 bendings), 1293 m (NH bending) and 755 m cm^{-1} (CS stretching). Main bands for $[Re(Me_2tu)_6](PF_6)_3$: 3388 s and 3299 s (in and out of plane NH stretchings), 2958 w and 2850 vw (symmetric and asymmetric CH_3 stretchings), 1606 s (combination mode of CN stretching and *trans* NH bending), 1527 s (combination mode of CN stretching and *cis* NH bending), 1482 w and 1450 w (symmetric and asymmetric CH_3 bendings) and 715 m cm^{-1} (mainly CS stretching). Main bands for $[Re(Ettu)_6](PF_6)_3$: 3371 s, 3310 s and 3271 s (NH and symmetric and asymmetric NH_2 stretchings), 2989 vw and 2850 vw (symmetric and asymmetric CH_3 stretchings), 1636 s (NH_2 bending), 1575 s (combination mode of CN and CS stretchings and NCN bending), 1509 s (CN asymmetric stretching), 1459 w (CH_3 bending) and 776 m cm^{-1} (CS stretching). The s, m, w and vw symbols denote strong, medium, weak and very weak bands respectively. Decrease in CS stretching frequencies and all the other changes observed for the complexes compared to the free ligands agree with S-bonding to the rhenium atom [25,34,35]. New bands at 341 cm^{-1} for $[Re(Me_2tu)_6](PF_6)_3$, at 351 cm^{-1} for $[Re(Metu)_6](PF_6)_3 \cdot H_2O$ and at 337 cm^{-1} for $[Re(Ettu)_6](PF_6)_3$ can be tentatively assigned to Re–S stretching modes even though low-frequency data were not reported for other Re thiourea complexes.

Decomposition of $[Re(Ettu)_6]Cl_3$, $[Re(Metu)_6]Cl_3$ and $[Re(Me_2tu)_6]Cl_3$ in water proceeds with lowering of the intense yellow color of their solutions. ReO_2 is the resulting product. Decomposition reaction has a first order dependence on complex concentration, in all tested conditions. Stability improves around pH 1.3–2.0 for $[Re(Metu)_6]Cl_3$ and $[Re(Me_2tu)_6]Cl_3$ and around pH 2.0–3.0 for $[Re(Ettu)_6]Cl_3$. As pH increases, oxidation occurs with increasing rate. At constant pH, decomposition takes place according to the following rate order: $[Re(Metu)_6]Cl_3 < [Re(tu)_6]Cl_3 \ll [Re(Me_2tu)_6]Cl_3$ as showed in Fig. 1 and Table 3. $[Re(Ettu)_6]Cl_3$ decomposes more slowly than the others at pH values higher than 2.0. Therefore kinetics of decomposition in aqueous media depends on pH and also on ligand nature.

Decomposition reactions in methanol show also a first order dependence on complex concentration. Decomposition takes place more slowly in methanol than in aqueous media (pH values above 2). The complexes decompose in methanol according to the following rate order: $[Re(Ettu)_6]Cl_3 < [Re(Metu)_6]Cl_3 \ll [Re(Me_2tu)_6]Cl_3$.

So, decomposition by oxidation of the precursors would compete with substitution of thiourea or alkylthioureas by other ligands more or less efficiently depending on the experimental conditions selected [26]. Owing to this competition, substitution in aqueous solution should be tried in acidic media despite the fact that the chelating capability of incoming ligands usually increases with pH. Therefore, syntheses of new Re compounds by substitution onto these complexes should be tried in methanolic media in order to minimize simultaneous oxidation of the starting material. Such substitution experiments in methanolic medium onto $[Re^{III}L_6]^{3+}$ complexes, with L=tu, Ettu, Metu or Me_2tu and dppe as incoming ligand, lead to the already known $[Re^{III}(dppe)_2Cl_2]Cl.2MeOH$ with good yield. Substitution onto the same starting compounds with dppp as incoming ligand leads to $[Re^{III}(dppp)_2Cl_2]Cl$ in high yield. This complex has been previously reported but not fully characterized [36]. A comparison between the four starting complexes was performed in terms of substitution rate and yield of the substitution. Results with dppe and dppp as incoming ligands show similar trends. As

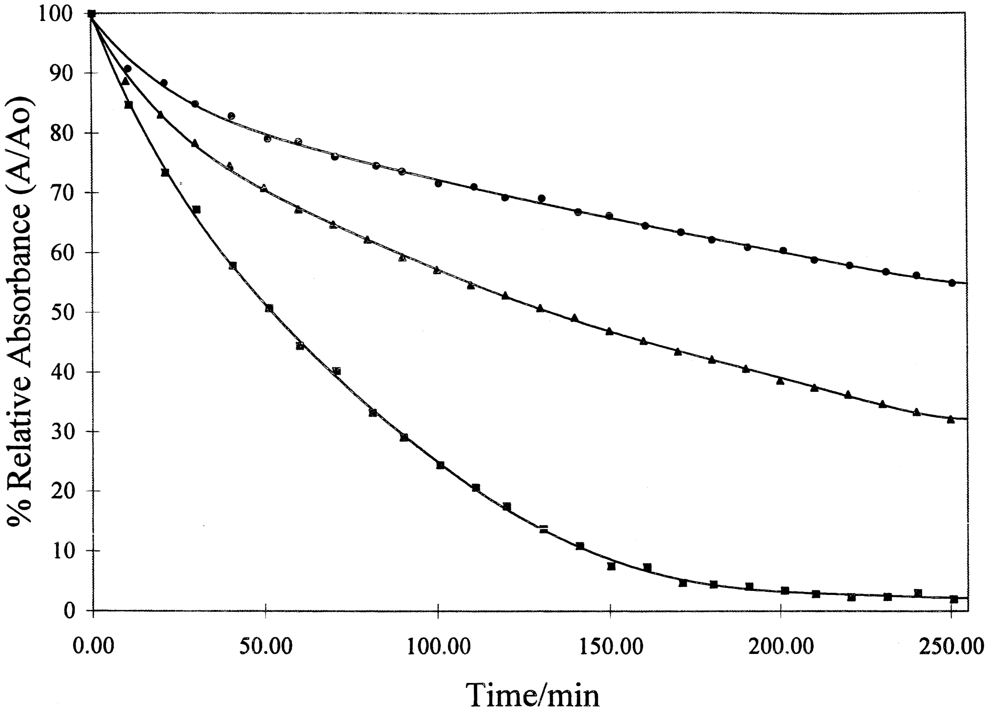

Fig. 1. Decomposition at 25.0°C of $[Re(tu)_6]Cl_3$, $[Re(Metu)_6]Cl_3$ and $[Re(Me_2tu)_6]Cl_3$ 10^{-4} M aqueous solutions at pH 1.6: -●- $[Re(Metu)_6]Cl_3$; -▲-, $[Re(tu)_6]Cl_3$; -■-; $[Re(Me_2tu)_6]Cl_3$.

shown in Table 1, $[Re(Me_2tu)_6]^{3+}$ seems to be a good precursor despite being the least stable of the series. $[Re(Metu)_6]^{3+}$ and $[Re(Ettu)_6]^{3+}$ seem to be the best precursors, leading faster to a complete substitution and with the highest yield. So, having in mind measured times to complete substitution, yields and decomposition rates of the precursors, Re(III) complexes with thiourea and alkylthioureas can be ordered according to their substitution rate as follows: $[Re(tu)_6]^{3+} < [Re(Ettu)_6]^{3+} \cong [Re(Metu)_6]^{3+} < [Re(Me_2tu)_6]^{3+}$. These results agree with those reported on ligand substitution rate constants of $[Tc(alkylthiourea)_6]Cl_3$ by pyrimidine-thione derivatives: $[Tc(tu)_6]Cl_3 < [Tc(Metu)_6]Cl_3 < [Tc(Me_2tu)_6]Cl_3$[9]. Then, substitution kinetics for these Re complexes depend on leaving ligand nature as stated for the Tc(III) analogues.

A new easy procedure has been developed to lead to low valent Re complexes in high yield. This new route relies upon the labile Re(III) thioureas complexes as preparative intermediates. This new family of precursors shows some interesting features. Precursors can be easily prepared in high yields. Moreover, salts of these starting complexes with different counterions can be isolated. Taking into account solubilities, the selection of the appropriate salt of the precursor offers the possibility of performing ligand substitution reactions with a wide range of incoming ligands by working in different media. $[Re(Metu)_6]^{3+}$ seems to be the best precursor of the series since the synthesis of the ethylthiourea complex does not lead to easily isolable compounds and the synthesis of the Me_2tu analog leads to relatively low yields. In addition, the Metu complex shows higher ligand substitution rates than $[Re(tu)_6]^{3+}$.

3.1. Molecular structure of hexakis (N-ethylthiourea) rhenium (III) trihexafluorophosphate

Selected bond distances and angles are given in Tables 4 and 5. Fig. 2 is an ORTEP drawing of the compound

Table 3
Stability at 25.0°C in aqueous media at different pH values, and in methanol for $[Re(Ettu)_6]Cl_3$, $[Re(Metu)_6]Cl_3$ and $[Re(Me_2tu)_6]Cl_3$

$[Re(Metu)_6]Cl_3$			$[Re(Ettu)_6]Cl_3$			$[Re(Me_2tu)_6]Cl_3$		
Solvent	pH	$t_{50\%}$ [a]	Solvent	pH	$t_{50\%}$ [a]	Solvent	pH	$t_{50\%}$ [a]
Water	1.3	360	Water	2.2	287	Water	1.5	64
Water	2.0	74	Water	2.7	190	Water	2.0	41
Water	2.7	13	Water	3.0	43	Water	2.2	26
MeOH	–	260	MeOH	–	560	MeOH	–	35

[a] $t_{50\%}$ is the time of 50% decomposition for each complex, in minutes.

Table 4
Selected interatomic bond distances (Å) for $[Re(Ettu)_6](PF_6)_3$ and $[Re(Me_2tu)_6](PF_6)_3$ (e.s.d.'s in parentheses)

	$[Re(Ettu)_6](PF_6)_3$	$[Re(Me_2tu)_6](PF_6)_3$
Re–S(1)	2.432(4)	2.423(3)
Re–S(2)	2.420(4)	2.416(3)
Re–S(3)	2.419(4)	2.446(3)
Re–S(4)	2.402(4)	2.431(3)
Re–S(5)	2.422(3)	2.429(3)
Re–S(6)	2.441(4)	2.417(3)
S(1)–C(1)	1.72(2)	1.732(13)
S(2)–C(2)	1.74(2)	1.735(14)
S(3)–C(3)	1.75(2)	1.75(2)
S(4)–C(4)	1.70(2)	1.725(13)
S(5)–C(5)	1.76(2)	1.744(11)
S(6)–C(6)	1.75(2)	1.719(12)
C(1)–N(11)	1.33(2)	1.286(14)
C(1)–N(12)	1.37(3)	1.35(2)
C(2)–N(21)	1.30(2)	1.33(2)
C(2)–N(22)	1.32(2)	1.31(2)
C(3)–N(31)	1.36(2)	1.31(2)
C(3)–N(32)	1.32(2)	1.36(2)
C(4)–N(42)	1.32(2)	1.31(2)
C(4)–N(41)	1.34(2)	1.33(2)
C(5)–N(52)	1.30(2)	1.31(2)
C(5)–N(51)	1.30(3)	1.31(2)
C(6)–N(62)	1.28(3)	1.319(14)
C(6)–N(61)	1.33(2)	1.323(14)

Table 5
Selected bond angles (°) for $[Re(Ettu)_6](PF_6)_3$ and $[Re(Me_2tu)_6](PF_6)_3$ (e.s.d.'s in parentheses)

	$[Re(Ettu)_6](PF_6)_3$	$[Re(Me_2tu)_6](PF_6)_3$
S(1)–Re–S(2)	179.8(2)	178.62(11)
S(1)–Re–S(3)	98.34(13)	84.07(12)
S(1)–Re–S(4)	81.16(14)	96.83(12)
S(1)–Re–S(5)	82.78(13)	98.82(11)
S(1)–Re–S(6)	97.93(13)	80.34(11)
S(2)–Re–S(3)	81.54(14)	96.08(12)
S(2)–Re–S(4)	98.95(13)	83.04(12)
S(2)–Re–S(5)	97.44(14)	82.52(11)
S(2)–Re–S(6)	81.85(14)	98.31(11)
S(3)–Re–S(4)	179.1(2)	178.72(11)
S(3)–Re–S(5)	99.17(13)	98.45(12)
S(3)–Re–S(6)	80.39(13)	81.16(12)
S(4)–Re–S(5)	81.49(14)	80.52(11)
S(4)–Re–S(6)	98.96(14)	99.88(10)
S(5)–Re–S(6)	179.20(12)	179.11(11)
C(1)–S(1)–Re	116.0(6)	116.4(4)
C(2)–S(2)–Re	115.2(6)	115.5(5)
C(3)–S(3)–Re	116.8(5)	113.8(7)
C(4)–S(4)–Re	114.9(6)	116.3(5)
C(5)–S(5)–Re	116.3(7)	114.5(5)
C(6)–S(6)–Re	115.8(7)	116.1(4)
N(11)–C(1)–N(12)	121(2)	119.4(12)
N(11)–C(1)–S(1)	118.7(13)	119.7(11)
N(12)–C(1)–S(1)	120.5(11)	120.9(9)
N(22)–C(2)–N(21)	122(2)	120.0(14)
N(22)–C(2)–S(2)	13.3(14)	119.6(13)
N(21)–C(2)–S(2)	124.9(13)	120.4(11)
N(31)–C(3)–N(32)	121(2)	120(2)
N(31)–C(3)–S(3)	122.1(12)	122(2)
N(32)–C(3)–S(3)	116.7(12)	118(2)
N(42)–C(4)–N(41)	118(2)	117.7(12)
N(42)–C(4)–S(4)	125.2(13)	122.6(11)
N(41)–C(4)–S(4)	117(2)	119.7(10)
N(52)–C(5)–N(51)	121(2)	120.5(11)
N(52)–C(5)–S(5)	115(2)	119.0(11)
N(51)–C(5)–S(5)	124.5(12)	120.4(10)
N(62)–C(6)–N(61)	124(2)	118.7(11)
N(62)–C(6)–S(6)	121.3(14)	118.5(10)
N(61)–C(6)–S(6)	115(2)	122.6(9)

showing the labeling of the non-hydrogen atoms and their vibrational ellipsoids [37].

3.2. Molecular structure of hexakis (N,N′-dimethylthiourea) rhenium (III) trihexafluorophosphate

Selected bond distances and angles are given in Tables 4 and 5. Fig. 3 is an ORTEP drawing of the compound showing the labeling of the non-hydrogen atoms and their vibrational ellipsoids [37].

3.3. Discussion of structural results

The X-ray diffraction results show that both new complexes consist of discrete monomeric molecules. The coordination polyhedra around the Re(III) ion are distorted octahedra. The six alkylthiourea ligands are sulfur bonded to the central atom. Though *trans* S–Re–S angles are close to 180° [varying from 178.6(1) to 179.1(1)° for $[Re(Me_2tu)_6](PF_6)_3$ and from 179.1(2) to 179.8(2)° for $[Re(Ettu)_6](PF_6)_3$], there are appreciable departures from ideal octahedral symmetry. The *cis* S–Re–S angles differ significantly from 90° [vary from 80.3(1) to 99.9(1)° for $[Re(Me_2tu)_6](PF_6)_3$ and from 80.4(1) to 99.2(1)° for $[Re(Ettu)_6](PF_6)_3$]. The Re–S bond distances vary from 2.416(3) to 2.446(3) Å [average of 2.43(1) Å] for $[Re(Me_2tu)_6](PF_6)_3$ and from 2.402(4) to 2.441(4) Å [average of 2.42(1) Å] for $[Re(Ettu)_6](PF_6)_3$ within a maximum of five standard deviations of bond length errors. Re–S bond distances lay in the wide range of Re–S lengths reported for other six-coordinate rhenium complexes and are quite similar to those reported for $[Re(tu)_6]Cl_3.4H_2O$. In contrast to $[Re(tu)_6]Cl_3.4H_2O$ both complexes show a set of six different Re–S distances [25].

Similar departures from perfect octahedral coordination have also been observed in $[Tc(Me_2tu)_6](PF_6)_3$, $[Tc(Metu)_6](PF_6)_3\cdot H_2O$ and $[Tc(tu)_6]Cl_3.4H_2O$. Possible reasons for these distortions have been previously discussed, including Jahn-Teller effect and ligand–ligand repulsion [6,25].

The Re–S–C bond angles are slightly greater than the tetrahedral value, varying from 113.8(7) to 116.4(4)° for the dimethylthiourea complex and from 114.9(6) to 116.8(5)° for the ethylthiourea complex. The S–C–N angles are in the range from 118(2) to 123(1)° for $[Re(Me_2tu)_6](PF_6)_3$ as expected for a C(sp^2) bonding. The

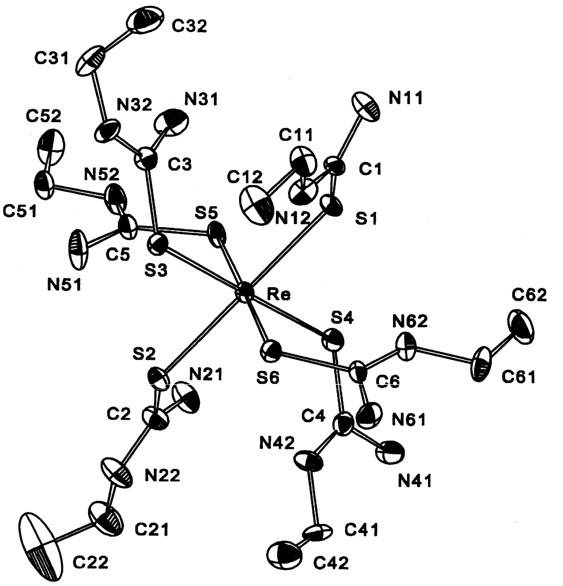

Fig. 2. ORTEP view of $[Re(SC(NH_2)NHCH_2CH_3)_6]^{3+}$ ion in $[Re(Ettu)_6](PF_6)_3$ showing the labeling of the non-hydrogen atoms and their vibrational ellipsoids at 20% probability.

variation in S–C–N angles is greater for $[Re(Ettu)_6](PF_6)_3$, from 113(1) to 125(1)°.

The $S{=}C(NC_{methyl})_2$ and $S{=}CN_2C_{ethyl}$ groups are planar to within experimental accuracy, while in $[Re(Ettu)_6](PF_6)_3$ the methyl carbons separations from the corresponding least-squares planes vary from 0.04(2) Å for ligand labeled 5 to 1.30(2) Å for ligand 3. Average S–C and C–N bond lengths are 1.74(1) and 1.32(2) Å for $[Re(Me_2tu)_6](PF_6)_3$ and 1.74(2) and 1.32(2) Å for $[Re(Ettu)_6](PF_6)_3$, respectively, in agreement with corresponding values for $[Re(tu)_6]Cl_3{\cdot}4H_2O$ [mean S–C and C–N distances of 1.746(8) and 1.32(1) Å respectively [25]] and for $[Tc(Me_2tu)_6](PF_6)_3$ [mean d(S–C)=1.73(1) Å and mean d(C–N)=1.34(2) Å[12]]. The N–CH_3 bond lengths in $[Re(Me_2tu)_6](PF_6)_3$ vary from 1.44(2) to 1.48(2) Å [mean d(C–N)=1.46(1) Å] as observed in $[Tc(Me_2tu)_6](PF_6)_3$. In $[Re(Ettu)_6](PF_6)_3$ mean N–C(ethyl) and ethyl C–C bond distances are 1.47(3) and 1.47(5) Å, respectively. In this structure the increasing dispersion in bond lengths towards the ligand ethyl free end is a consequence of librational disorder.

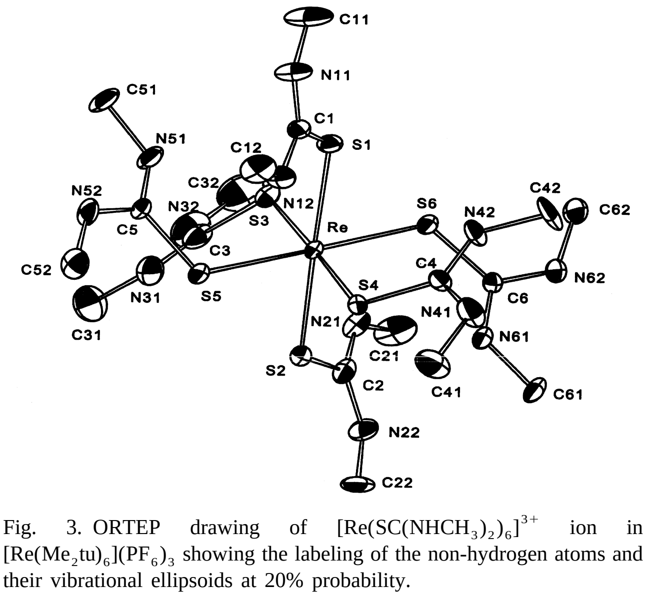

Fig. 3. ORTEP drawing of $[Re(SC(NHCH_3)_2)_6]^{3+}$ ion in $[Re(Me_2tu)_6](PF_6)_3$ showing the labeling of the non-hydrogen atoms and their vibrational ellipsoids at 20% probability.

The C–N bonds of thiourea derivatives have an evident double bond character. Therefore *N*-alkylthioureas can exist in different configurations where the thioamide H atom and the thiocarbonyl bonds are either *cis* or *trans* [12]. For the described ethylthiourea compound the six ethylthiourea ligands have the *cis* configuration. The ethyl groups are oriented away from the Re atom. In $[Re(Me_2tu)_6](PF_6)_3$ all the dimethylthiourea ligands have the *cis–trans* configuration as in the free ligand.

Similarly to the other thiourea and alkylthioureas Re and Tc compounds, the arrangement of the dimethylthiourea and ethylthiourea ligands around rhenium atom results from a compromise between steric hindrance and the tendency of the $ReSC(NC_{methyl})_2$ or $ReSCN_2C_{ethyl}$ groups to be as planar as possible. In $[Re(Me_2tu)_6](PF_6)_3$ the rhenium atom departs from the least-squares planes through the $S{=}C(NC_{methyl})_2$ groups in distances that range from 0.050(1) Å for ligand 6 to 1.157(1) Å for ligand 3. In $[Re(Ettu)_6](PF_6)_3$ the rhenium atom departs from the least-squares planes through the S=CN(NC) groups in distances that range from 0.045(4) Å for ligand 5 to 0.640(4) Å for ligand 1.

As reported for $[Tc(Me_2tu)_6](PF_6)_3$ and $[Tc(Metu)_6](PF_6)_3.H_2O$, the PF_6^- ions in both structures present appreciable rotational disorder as shown by the relatively large displacement parameters of F atoms [12]. The corresponding observed bond distances and angles are therefore strongly distorted, with P–F lengths varying for example for $[Re(Me_2tu)_6](PF_6)_3$ from 1.45(1) to 1.62(1) Å (average d(P–F)=1.53(4) Å) and *cis* F–P–F angles ranging from 85(1) to 96(1)°.

Supplementary data

Listings of atomic fractional coordinates and equivalent isotropic temperature parameters, anisotropic thermal parameters, hydrogen atoms positions and calculated as well as observed structure factor amplitudes of both reported structures are available as supplementary data. Cambridge Crystallographic Data Centre codes are: 102605 for hexakis (N,N′-dimethylthiourea-S) rhenium(III) tri (hexafluorophosphate) and 102606 for hexakis(*N*-ethylthiourea-S) rhenium(III) tri(hexafluorophosphate).

Acknowledgements

This work was partially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICYT) and PNUD-UNESCO (Programa de Desarrollo de las Ciencias Básicas) of Uruguay, The Third World Academy of Sciences and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) of Argentina. The X-ray diffraction experiments were carried out at the National Diffraction Laboratory (LANADI), La Plata, Argentina. We are grateful to the government of Japan for the donation of the TGA and DTA Shimadzu analyzers.

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