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Synthesis, characterization and crystal structure of hexakis-(thiourea-S) rhenium(III) trichloride tetrahydrate: A potential precursor to low-valent rhenium complexes

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Abstract—A new rhenium(III) complex, $[Re(SC(NH_2)_2)_6]^{3+}$, has been prepared by reduction of perrhenate with tin chloride in strongly acidic solution in the presence of thiourea. The complex has been characterized in solution and the solid state by elemental and thermal analyses, electronic and IR spectroscopy, conductimetric measurements, EPR spectra and cyclic voltammetry. Stability in aqueous solution was tested spectrophotometrically. The molecular structure of the complex in the $[Re(tu\text{-}S)_6]Cl_3 \cdot 4H_2O$ salt was determined by X-ray diffraction. The compound is isomorphous to $[Tc(tu\text{-}S)_6]Cl_3 \cdot 4H_2O$. The rhenium ion, sited at an inversion center, is quasi-octahedrally coordinated by six thiourea sulfur atoms [*d*(Re—S) vary from 2.412(2) to 2.429(2) Å]. Average thiourea bond distances are similar to those observed for the Tc analog [*d*(S—C) = 1.746(8) and *d*(C—N) = 1.32(1) Å]. © 1997 Published by Elsevier Science Ltd

Keywords: rhenium(III); thiourea complex; $[Re(thiourea\text{-}S)_6Cl_3 \cdot 4H_2O$ structure.

Technetium and rhenium chemistry has been a major focus of interest in inorganic chemistry in recent years. This is due to the extensive use of the γ-emitter ^{99m}Tc in diagnostic nuclear medicine and also to the potential usefulness of the β^--emitters ^{186}Re and ^{188}Re for radiotherapeutic purposes [1–4]. These applications have renewed the interest in exploring rhenium chemistry and the Re–Tc chemical analogy. Due to this interest in correlating Tc and Re chemistry, a growing number of studies comparing properties of Tc and Re analogs have recently been published, especially involving Tc^V and Re^V complexes [5–9].

The syntheses of Re^{III} complexes described in the literature are mainly based on substitutions in the *trans*-$[ReCl_3(NCCH_3)(PPh_3)_2]$ precursor, which usually lead to mixed-ligand neutral species [10]. On the other hand, the $[Tc^{III}(SC(NH_2)_2)_6]Cl_3$ salt, where $SC(NH_2)_2$ is thiourea (tu), has been extensively used as a convenient starting compound for other low-valent Tc complexes, due to the easy replacement of the thiourea ligands under mild conditions. Monodentate thiourea can be easily substituted by polydentate ligands, giving compounds with higher thermodynamic stability [9,11–14].

The Tc–thiourea complex has been isolated and its structure elucidated by X-ray diffraction methods [11]. However, so far its rhenium analog has neither been obtained in the solid state nor fully characterized. Attempts to synthesize rhenium thiourea complexes produced Re^V oxo or dioxo mixed-ligand complexes or the neutral Re^{III} species $[Re(tu)_3Cl_3]$. Most of these

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products remain incompletely characterized, since they were not subjected to X-ray crystal structure analyses [15,16]. Bandoli *et al.* [9] briefly reported the synthesis of Re^{III} complexes by ligand substitution onto $[Re(tu)_6]Cl_3$ without giving details of the synthesis and characterization of the starting complex.

The $[Tc(tu)_6]^{3+}$ complex has been prepared by reducing pertechnetate with excess thiourea in alcoholic acidic media [11]. In this case the ligand is also the reducing agent. Perrhenate is more difficult to reduce than pertechnetate [15] and $[Re(tu)_6]^{3+}$ cannot be prepared in the same way as its Tc analogue.

We present here results on the synthesis, molecular structure, spectroscopic properties and chemistry of the $[Re(tu)_6]^{3+}$ complex ion, which may be a potential precursor to further low-valent rhenium complexes by ligand substitution. Furthermore, comparison with known analogous Tc compounds is expected to contribute to a better understanding of Re^{III}–Tc^{III} chemical similarities.

EXPERIMENTAL

Preparation of hexakis(thiourea-S)rhenium(III) *trichloride*

All common laboratory chemicals were purchased from commercial sources and used without further purification. $SnCl_2 \cdot 2H_2O$ (200 mg, 0.89 mmol) was dissolved in 2 N HCl (5 cm^3). Immediately after the addition of 1.1g (14.5 mmol) of thiourea (tu) and 100 mg (0.37 mmol) of NH_4ReO_4, a white powder suspension in a dark red–brown colored solution was obtained. The color of the reaction mixture gradually changed to dark yellow–brown. The suspension was stirred over 6 h at room temperature and filtered. After keeping the filtrate at -5°C overnight, a dark orange–brown solid was precipitated. The complex was isolated by centrifugation and washed with acetone. Recrystallization was performed dissolving the complex in an *ca* 0.2 M thiourea solution in 2 N HCl and storing the solution overnight at -5°C. Yield after recrystallization was around 50%. M.p. = 188°C (dec). The deep red crystals, washed with acetone, were suitable for X-ray analysis. Other characterizations were performed after grinding and drying the sample *in vacuo*. The complex could also be isolated by adding a high volume of acetone to the initial dark solution obtained after filtering off the white suspended powder. The complex is very soluble in water, moderately soluble in ethanol and methanol and insoluble in acetone.

After grinding and drying the solid *in vacuo* thermal analyses (TGA and DTA) results showed that only one water molecule of crystallization remained. Elemental analyses were performed on another portion of this dried sample. Found: C, 9.6; H, 3.4; N, 22.0; S, 25.7; Re, 23.0. Calc. for: $C_6H_{26}N_{12}S_6ORe$: C, 9.4; H, 3.4; N, 21.9; S, 25.1; Re, 24.2.

Characterization

C, H, N and S elemental analyses were performed on an elemental analyser Carlo Erba Model EA 1108, attached to an Eager 200 data system. Rhenium was determined spectrophotometrically by reaction with α-furyldioxime [17].

Thermogravimetric analysis (TGA) was performed on a TGA-50 Shimadzu analyser with a 50 cm^3 min^{-1} N_2 flow and a heating rate of 6°C min^{-1} up to 300°C. Differential thermal analysis (DTA) was carried out on a DTA-50 Shimadzu analyser with calcined Al_2O_3 as reference, 10°C min^{-1} heating rate and 50 cm^3 $min^{-1}N_2$ flow.

UV–vis spectra were recorded on a Spectronic 3000 spectrophotometer, with ethanol or water as solvents.

FTIR spectra (4000–400 cm^{-1}) were measured as KBr pellets on a Bomem M-102 instrument.

Powder EPR data were obtained with a Varian E-109 spectrometer using a Variant E231 rectangular cavity working in the TE102 mode at 9.7 GHz with a magnetic field modulation frequency of 100 KHz. EPR spectra in the 100–300 K range were recorded employing a Varian E257-X variable temperature controller.

Conductimetric measurements were performed at 25°C in 10^{-3} M aqueous solution (extrapolated to zero time to correct for slow decomposition during the measurements).

Preliminary kinetic stability studies of $[Re(tu)_6]Cl_3$ were carried out in aqueous solution (10^{-3}–10^{-4} M), pH range 0–6 and pH 8 and temperature range 20–60 °C. Decomposition in the different conditions tested (fixed initial concentration, temperature and pH) was followed spectrophotometrically by measuring periodically the absorbance of the solution at 393 nm (one of the absorption maxima of $[Re(tu)_6]Cl_3$ aqueous solutions). Constant temperature was continuously controlled by a Peltier device. For a fixed set of conditions, % remaining Re–tu complex at each reaction time was determined as the quotient of measured absorbance at 393 nm at this time and initial absorbance at the same wavelength.

Cyclic voltammograms in aqueous solutions were obtained with a Metrohm glassy-carbon working electrode versus Ag/AgCl (KCl 3M). A Pt wire was used as the auxiliary electrode. A PGP 201 potentiostat (Radiometer Copenhagen) was employed as the electrochemical controller. Data were processed using the Voltamaster 1 software [5]. All potentials were referred to the standard hydrogen electrode (SHE). Voltammograms were recorded on nitrogen-purged aqueous solutions (pH 2.4–4.2), which contained *ca* 1 mM electroactive species, using 0.5 M KCl as the supporting electrolyte. Outside this pH range measurements were not possible owing to fast decomposition. Voltammograms of 1 mM thiourea solutions (pH 1.8–6.0) were also performed. Scans were carried out at rates between 50 and 500 mV

min^{-1}. All experiments were performed at room temperature (25 ± 2°C).

X-ray diffraction data and crystal structure determination and refinement

Crystal data, data collection procedure, structure determination methods and refinement results are summarized in Table 1. All hydrogen atoms, except those of a disordered water molecule around an inversion center, were found in a difference Fourier map and included in the final refinement as fixed contributors with two independent isotropic temperature parameters; one common to the amine hydrogens and the other one common to the water hydrogen atoms. They converged in the final refinement cycle to $U = 0.063(8)$ [$B = 4.9(6)$] and $U = 0.09(2)$ Å^2 [$B = 7(2)$ Å^2], respectively.

RESULTS AND DISCUSSION

Reduction of ReO_4^- by stannous chloride in strongly acidic solution in the presence of excess thiourea, according to the experimental conditions described, leads to the formation of $[Re(tu)_6]Cl_3 \cdot 4H_2O$ in good yield. The reaction proceeds *via* a red violet intermediate which shows a single broad absorption band at 490 nm with a relatively low extinction coefficient.

Table 1. Crystal data and summary of intensity data collection and structure refinement for $[Re(SC(NH_2)_2)_6]Cl_3 \cdot 4H_2O$

Formula	$[Re(SC(NH_2)_2)_6]Cl_3 \cdot 4H_2O$
Color/shape	Deep red/parallelepid
Formula weight	821.36
Space group	*C*2/*c*
Temperature (°C)	22
Cell constants[a]	
a(Å)	11.829(2)
b(Å)	12.046(3)
c (Å)	19.606(2)
β (°)	95.30(1)
Cell volume (Å^3)	2781.9(8)
Formula units/unit cell	4
D_{calc} (g cm^{-3})	1.922
μ_{calc} (cm^{-1})	51.4
Diffractometer/scan	Enraf–Nonius CAD-4/ω–2θ
Radiation, graphite monochromator	Mo-K_α ($\lambda = 0.71069$ Å)
Maximum crystal dimension (mm)	0.05 × 0.20 × 0.44
Scan width	$0.8 + 0.35 \tan \theta$
Standard reflections	(8,0,0); (0,0,12)
Decay of standards (%)	±1
Reflections measured	3614
2θ range (°)	$2 \leqslant 2\theta \leqslant 59.93$
Range of *h*, *k*, *l*	±16, +16, +27
Reflections observed [$F_0 \geqslant 6\sigma(F_0)$][b]	2875
Data reduction and correction[c] and structure solution and refinement programs[d]	SDP [18], SHELX-76 [19], SHELX-86 [20]
No. of parameters varied	153
Minimized function	$\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2$
Weights, *w*	$[\sigma(F_0)^2 + 0.001\, F_0^2]^{-1}$
Goodness of fit, *S*	1.36
$R = \Sigma\lvert\lvert F_0\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_0\rvert$	0.037
$R_w = [\Sigma w(\lvert F_0\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_0\rvert^2]^{1/2}$	0.037
Largest feature final difference map (e Å^{-3})	1.9

[a] Least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 23 reflections in the $16.5 < 2\theta < 28.2°$ range.

[b] Corrections: Lorentz, polarization and absorption [21]. After this latter correction, the R_{sym} agreement factor among symmetry related reflections dropped from 0.052 to 0.038; the corresponding maximum and minimum transmission factors were 0.783 and 0.434.

[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] Located close to the rhenium atom position.

Probably a Re^{V} oxo thiourea complex is formed, analogous to the Tc^{V} intermediate detected in the reaction between pertechnetate and thiourea in a hydrochloric acid solution [22]. By working with a low reducing agent/Re molar ratio (around 1 : 1) practically only this red violet complex is obtained.

Thermal analyses (TGA, DTA) performed on a sample dried *in vacuo* of the Re^{III} complex show an endothermic weight loss of 2.5% centered at 152.5°C, corresponding to the loss of one water molecule of crystallization per complex ion (2.3% calc.). Around 188°C DTA shows an endothermic peak due to fusion. Above 188°C the complex decomposes with a total weight loss that almost corresponds to the loss of six thiourea molecules.

Conductimetric measurements (in aqueous 10^{-3} M solution) are in accordance with a 3 : 1 electrolyte ($\Lambda_{M\,25^{\circ}C} = 345$ S cm^2 mol^{-1}) and are consistent with results reported by Abrams *et al.* [11] for the Tc analog (in methanol).

The electronic spectrum in ethanol shows two intense bands in the 300–700 nm region with the higher energy band at 386 nm being the strongest ($a = 1.0 \times 10^4$ M^{-1} cm^{-1}); the other band has a maximum at 451 nm ($a = 6.9 \times 10^3$ M^{-1} cm^{-1}). These bands seem to be originated in charge transfer transitions, as suggested by their high molar extinction coefficients. The first band shows a shoulder at 410 nm, which is not noticeable in aqueous solution. The visible spectrum shows a band shape similar to that corresponding to the Tc–tu analogue in methanol, but shifted to higher frequencies [11]. The UV spectrum exhibits a strong band at 240 nm corresponding to a $\pi^* \leftarrow \pi$ transition of the thiourea ligands.

The FTIR spectrum (4000–400 cm^{-1}) shows main absorption bands at 3459(s), 3344(s), 3173(s), 1625(s), 1512(m), 1401(s), 1099(w), 679(s), 591(m), 540(m) and 474(m) cm^{-1}. The ambidentate thiourea ligand is potentially capable of binding *via* sulfur or nitrogen atom. There are at least three major stretching bands [ν(CS), ν(CN) and $\nu(NH_2)$] that are diagnostic of the binding mode of thiourea to metals [23]. The CS stretching vibration for uncomplexed thiourea at 730 cm^{-1} decreases to 679 cm^{-1} in $[Re(tu)_6]Cl_3$. Simultaneously the strong ν(CN) mode at 1473 cm^{-1} for unbounded thiourea appears at 1512 cm^{-1}, with reduced intensity, in the rhenium complex. Symmetric and asymmetric NH_2 stretching modes, which are detected as four strong bands at 3097, 3156, 3258 and 3365 cm^{-1} in the IR spectrum of the free ligand, are partially masked by the water molecules stretching bands in the 3500–3200 cm^{-1} region. Upon complexation, the free ligand absorption band at 1086 cm^{-1}, assigned to ν(NCN) and $\rho(NH_2)$ modes, suffers a substantial reduction in its intensity giving rise to the weak band observed at 1099 cm^{-1}. All these modifications are consistent with S-bonding to the rhenium atom. A similar spectroscopic behavior has been previously reported for the Tc analogue [11]. It is not surprising that the thiourea ligand is sulfur bonded to the Re^{III} or Tc^{III} atoms. As a result of the low formal charge of the central atom, it would preferably bond to the soft base part of the ligand, i.e. the sulfur atom. The absorption observed at 1625 cm^{-1} can be tentatively assigned to a NH_2 bending mode and the band at 1401 cm^{-1} to NCN stretching, NH_2 rocking and CS stretching modes [23]. The absence of characteristic absorptions of $ReO_2{}^+$, ReO^{3+} and μ-oxo species, which usually appear at around 830 cm^{-1} and in the 900–1000 cm^{-1} region, respectively, rules out the presence of these moieties [15].

The $[Re(tu\text{-}S)_6]^{3+}$ complex exhibits paramagnetic behavior, slightly dependent on temperature, down to *ca* 100 K. The EPR spectra indicate a gyromagnetic g-factor whose value increases from *ca* 2.14 at 100 K, reaches a maximum of 2.28 at *ca* 225 K and then drops to 2.14 at $T = 300$ K. These g values suggest a mainly spin contribution, as seems to be the case of the Tc analog where a magnetic moment of 2.7 μ_B at 308 K has been reported [11]. Both compounds are d^4 systems in a strong cubic ligand field giving rise, for perfect O_h symmetry, to the low-spin $(t_{2g})^4 : {}^3T_{1g}$ electronic ground state (see below).

Decomposition of $[Re(tu)_6]Cl_3$ in water proceeds with a diminution of the intense yellow color of the solution, producing perrhenate (detected by the appearance of its UV characteristic bands) and/or dispersed ReO_2, depending on initial concentration of the complex (10^{-4} and 10^{-3} M, respectively). A first-order dependance on complex concentration is observed. These preliminary stability studies also show an important dependence of decomposition kinetics on solution pH, as is shown in Fig. 1. Stability improves around pH 2–3. Outside this range decomposition takes place at a faster rate. At pH 8 and higher, oxidation is almost instantaneous. Decomposition takes place faster at higher temperature; at 40°C and pH 3 the complex decomposes completely in a few minutes. These considerations are relevant to substitution studies in progress, since decomposition by oxidation competes with substitution of thiourea by other ligands more or less efficiently, depending on the experimental conditions selected. Owing to decomposition, substitution in aqueous solution should be performed in acidic media. On the other hand, the chelating capability of incoming ligands usually increases at higher pH values. Therefore, for substitutions in aqueous solution optimal conditions for each incoming ligand should be carefully chosen, as reported for the Tc analogue [13,14].

To understand the stability results and to study the electrochemical behavior, cyclic voltammetric measurements were performed. A representative cyclic voltammogram of $[Re(tu)_6]Cl_3$ at pH 4.1 is shown in Fig. 2. The anodic scan consists mainly of two irreversible oxidation couples ($i_{pa} \gg i_{pc}$, i_{pa} and i_{pc} being the anodic and cathodic peak currents, respectively) with peaks at approximately $E_{a1} = 570$ mV and $E_{a2} = 820$ mV. Both signals are relative independent

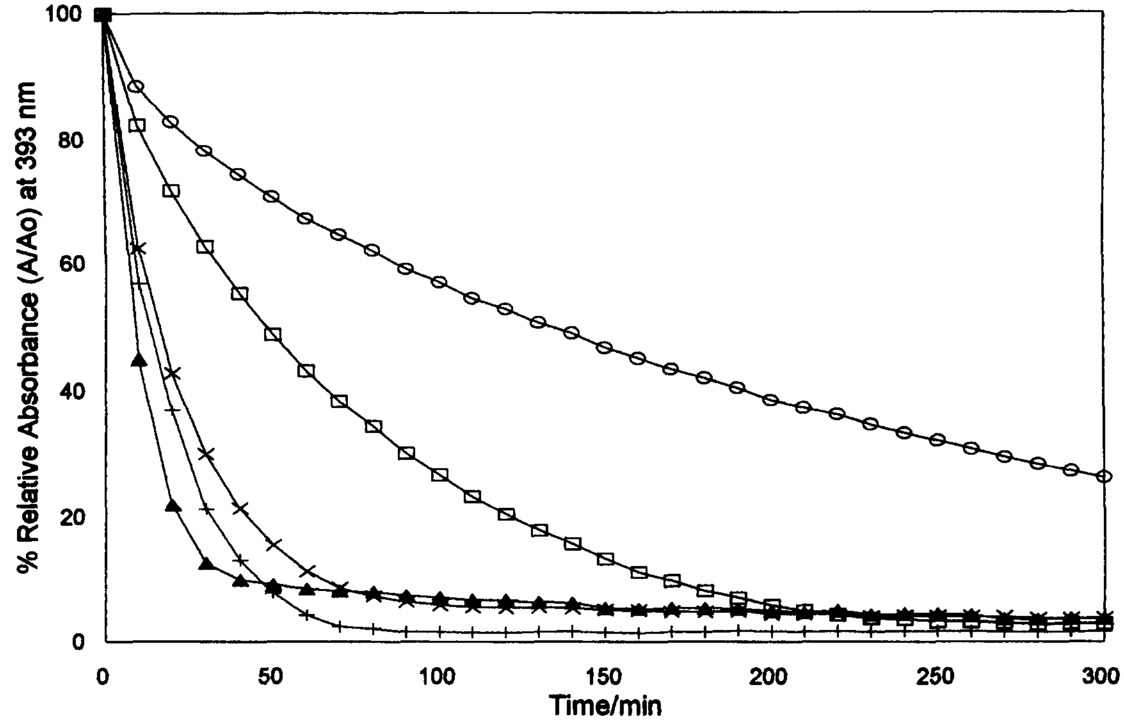

Fig. 1. Influence of pH on decomposition of $[Re(tu)_6]Cl_3$ 10^{-4} M aqueous solutions at 25°C, stated as remanent % Re–tu complex [determined as $(A/A_0)\%$ at 393 nm] versus time (min) at pH: 0.8, 1.6, 2.5, 3.4 and 5.2.

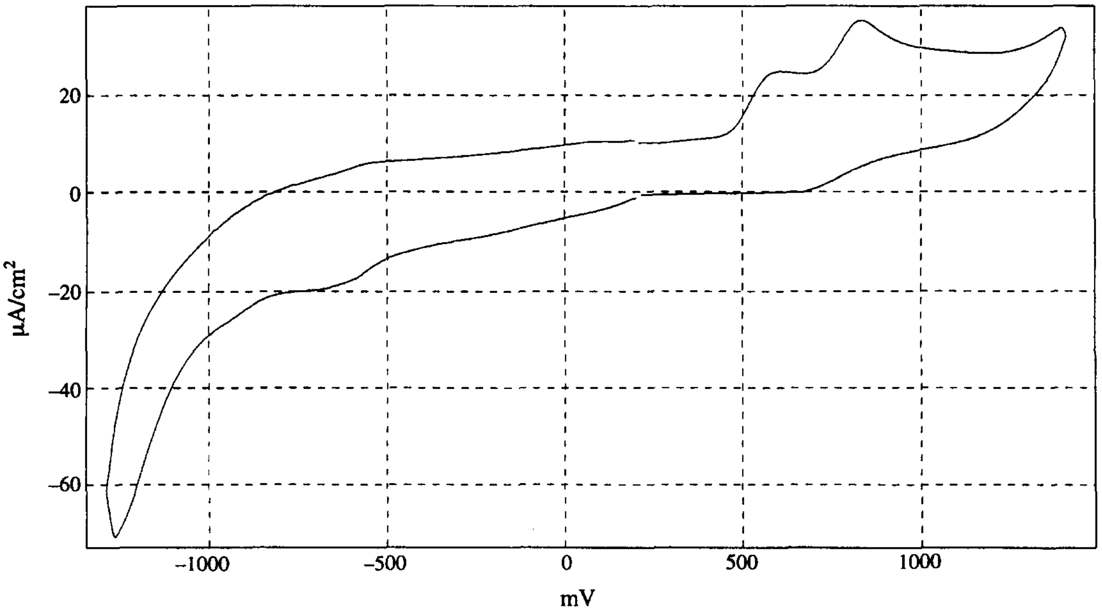

Fig. 2. A representative figure showing the cyclic voltammogram of $[Re(SC(NH_2)_2)_6]Cl_3$ (pH 4.1) at a scan rate of 300 mV min^{-1}.

of scan rate. Oxidation occurs at relatively mild potentials. From these experiments it is not possible to determine the number of electrons involved in the process. Voltammograms of thiourea aqueous solutions show mainly two irreversible oxidation peaks ($i_{pa} \gg i_{pc}$) at approximately 810 and 1350 mV, depending on scan rate, with a shape essentially independent of pH (in the tested pH range). The oxidation peak of thiourea at $E_a = 1350$ mV is not observed in the $[Re(tu)_6]Cl_3$ anodic scan. Therefore, both signals observed for the complex could be assigned to central atom oxidation. The pattern of the voltammograms and the E_a values are essentially independent of pH. Hence, the reason for the above different oxidation kinetics, strongly dependent on solution pH, does not seem to be linked to changes in thermodynamic properties. The cathodic branch shows a single irreversible peak at around $E_c = -630$ mV, owing to central atom reduction, since no signals are observed in the cathodic branch for the free ligand. This reduction peak is shifted significantly to more negative potentials as the pH value is lowered below 2.6.

Molecular structure of hexakisthiourea rhenium(III) *trichloride*

The X-ray diffraction study shows that the compound consists mainly of discrete monomeric molecules which crystallize with four molecules of water solvent. Relevant bond distances and angles are in Table 2. Figure 3 is an ORTEP [24] drawing of the compound showing the labeling of the atoms and their vibrational ellipsoids.

The rhenium atom, located at an inversion center, is in an approximately octahedral coordination with six sulfur atoms. There are appreciable departures from ideal octahedral symmetry. The S—Re—S angles differ significantly from 90° [vary from 81.54(5) to 99.35(5)°]. The Re—S distances vary from 2.412(2) to 2.429(2) Å within a maximum of 5.7 standard deviations of bond length errors. Similar departures from perfect octahedral coordination have also been observed in the isomorphous $[Tc(tu\text{-}S)_6]Cl_3 \cdot 4H_2O$ salt [11] and in $[Tc(Metu\text{-}S)_6](PF_6)_3 \cdot H_2O$, where Metu is methylthiourea [25]. Various possible reasons for these distortions have been considered, including the Jahn–Teller effect and ligand–ligand repulsion [11]. Re^{III} belongs to the group of 5*d* ions known to occur in "strong crystal field" octahedral coordination, including the isoelectronic Os^{IV} ion. Therefore, for perfect octahedral coordination it is to be expected that an orbitally degenerate $^3T_{1g}$ ground electronic state configuration exists. This is subjected to a Jahn–Teller effect that could remove the degeneracy by tetragonal and/or trigonal distortion. In fact, both distortions are present here; the short Re—S(3) bond corresponds to a tetragonal deformation and the S—Re—S angles differing significantly from ideal 90° points to a superimposed trigonal distortion.

Table 2. Interatomic bond distances (Å) and angles (°) for $[Re(SC(NH_2)_2)_6]Cl_3 \cdot 4H_2O$ (e.s.d.'s in parentheses)[a]

Re—S(1)	2.423(2)
Re—S(2)	2.429(2)
Re—S(3)	2.412(2)
S(1)—C(1)	1.736(8)
S(2)—C(2)	1.753(8)
S(3)—C(3)	1.750(8)
N(11)—C(1)	1.33(1)
N(12)—C(1)	1.33(1)
N(21)—C(2)	1.32(1)
N(22)—C(2)	1.32(1)
N(31)—C(3)	1.33(1)
N(32)—C(3)	1.32(1)
S(1)—Re—S(2)	85.33(5)
S(1)—Re—S(3)	99.35(5)
S(1)—Re—S(2′)	94.67(5)
S(1)—Re—S(3′)	80.65(5)
S(2)—Re—S(3)	98.46(5)
S(2)—Re—S(3′)	81.54(5)
Re—S(1)—C(1)	115.8(2)
Re—S(2)—C(2)	117.1(2)
Re—S(3)—C(3)	116.3(2)
S(1)—C(1)—N(11)	115.6(5)
S(1)—C(1)—N(12)	24.1(5)
N(11)—C(1)—N(12)	120.3(6)
S(2)—C(2)—N(21)	115.3(5)
S(2)—C(2)—N(22)	124.0(5)
N(21)—C(2)—N(22)	120.7(6)
S(3)—C(3)—N(31)	123.8(5)
S(3)—C(3)—N(32)	115.9(5)
N(31)—C(3)—N(32)	120.3(6)

[a] Primed atoms are related to corresponding unprimed ones through the inversion symmetry operation $(0.5 - x, 0.5 - y, -z)$.

Re—S bond distances are similar to Tc—S lengths in $[Tc(tu)_6]Cl_3 \cdot 4H_2O$, laying in the wide range of Re—S lengths reported for other six-coordinate rhenium complexes. As expected, they are significantly longer than the Re—S distances reported for Re^V oxo thiourea complexes [26,27].

The thiourea ligands are planar to within experimental accuracy. Average S—C and C—N bond distances of 1.746(8) and 1.32(1) Å, respectively, agree well with the corresponding structural data for the technetium analog [11]. Both complexes exhibit longer average C—S distances and shorter average C—N distances than the free ligand [28]. These results are consistent with the observed decrease of the C—S stretching frequency of thiourea due to complexation. As for the Tc compound, the arrangement of the thiourea ligands around rhenium atom results from a compromise between steric hindrance and the tendency of the $ReSCN_2$ group to be as planar as possible. The Re atom departs from the least-squares planes corresponding to each of the thiourea ligands labeled from 1 to 3 by 0.657(2), 0.348(2) and 0.014(2) Å, respectively. The best least-squares $ReSCN_2$ planes form a propeller-like structure, as seen down the molecule quasi-trigonal axis, with dihedral angles of 71.7(2), 52.4(2) and 55.9(1)°.

One of the chlorine ions and one of the water molecules are on the same crystallographic two-fold axis. Another water molecule is disordered around an inversion center. The crystal is, in part, stabilized by a net of bent N—H···Cl, H—H···Ow and Ow—H···Cl hydrogen bonds of medium to weak strength.

Supplementary material available. Listing of atomic coordinates and equivalent isotropic temperature parameters (Table 3), anisotropic thermal parameters (Table 4), hydrogen atoms positions (Table 5), and

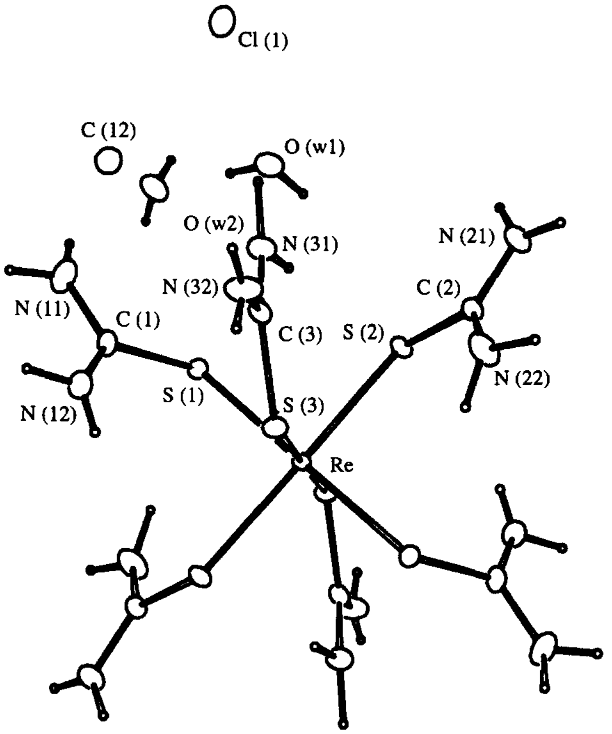

Fig. 3. ORTEP drawing of $[Re(SC(NH_2)_2)_6]Cl_3 \cdot 4H_2O$. The disordered water molecule at an inversion center is not included.

observed and calculated structure factor amplitudes (Table 6).

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