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The Thiourea Complexes of Rhenium and Technetium

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Received February 20, 1968

Ammonium perrhenate reacts with thiourea and stannous chloride to give several complexes according to the conditions used. Some complexes were isolated and their properties studied. The reactions of ammonium pertechnetate and thiourea are discussed by analogy.

Introduction

The solution complexes of technetium and rhenium with thiourea have been studied by several authors since 1955[1-7] but little is still known about their structure and composition. They were generally described as derivatives of the pentavalent and tetravalent metals. In a recent paper by Cotton *et al.*[8] the preparation and properties are reported of several rhenium-thiourea complexes, all of which contain the metal in the trivalent state. The I.R. spectrum of a compound described as $[Re(OH)_2(tu)_4]Cl_3 . 4H_2O$ has also been measured and discussed by Russian workers.[9]

Since the oxidation number of four is not very common among rhenium complexes[10-13] (with the exception of the hexahalogeno, hexacyano, hexathiocyanato, and few other derivatives) and since relatively little is known in general about rhenium complexes, we thought the problem worth of further investigation. Very recently several rhenium(IV)-nitrile complexes have been prepared by Rouschias and Wilkinson.[14]

Re^V-thiourea Complexes. By gradual addition of thiourea (tu) to hydrochloric acid solutions of NH_4ReO_4 and $SnCl_2$ in equimolar amounts, a blue complex absorbing around 600 mμ is initially formed. Increasing the concentration of tu the maximum of the absorption band is shifted continously towards lower wavelengths and increases in intensity, whilst the colour of the solution turns gradually pink-violet. A greater amount of tu is required to obtain the same shift in more concentrated HCl solutions. As an example a series of spectra measured in 4 N HCl is reported in Figure 1. With a ratio $[tu]/[Re] = 20$ the maximum of the absorption band is found at 530 mμ. In 6 N HCl the maximum is at 560 mμ, with the same ratio of ligand to metal ion. The spectra of the blue solutions show also a shoulder around 750 mμ, which becomes less pronounced when tu is added.

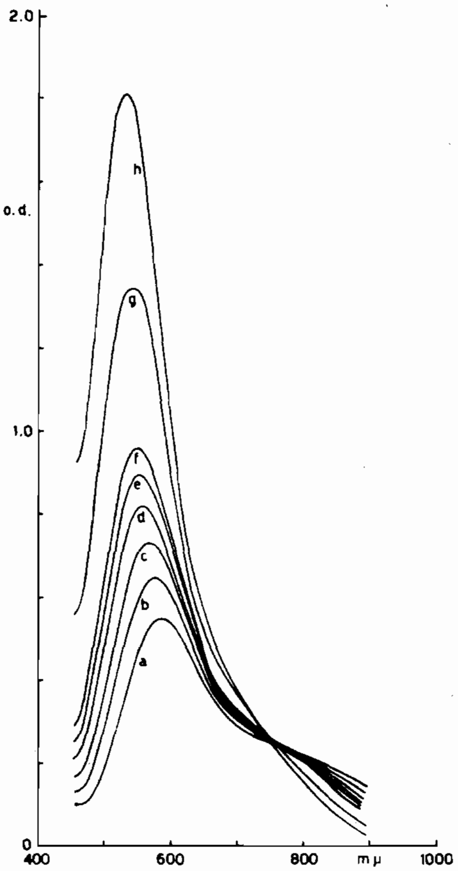

Figure 1. Absorption spectra of solutions containing NH_4ReO_4 0.5×10^{-2} *M*, $SnCl_2$ 0.5×10^{-2} *M*, HCl 4 N, and tu: a, 1.0×10^{-2} *M*; b, 1.2×10^{-2} *M*; c, 1.4×10^{-2} *M*; d, 1.6×10^{-2} *M*; e, 1.8×10^{-2} *M*; f, 2.0×10^{-2} *M*; g, 4.0×10^{-2} *M*; h, 10×10^{-2} *M*.

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From the pink-violet solutions containing excess tu a greenish crystalline precipitate is obtained on standing. No precipitate can be separated from the blue solutions. The results of the analysis are not reproducible for products precipitated from 2 N HCl, but when 6 N HCl is used they agree reasonably well with the formula $ReO(tu)_4Cl_3 . H_2O$(I). Accordingly a band is found in the infrared spectrum (Table I) at 950 cm^{-1}, that is in the region where compounds containing the Re=O group usually absorb.[15] The molecule of water of crystallization is lost very easily in oven at 60-80°C and partially by standing in a vacuum desiccator at room temperature (25-30°C). The compound is diamagnetic and its reflectance spectrum is reported in Figure 2a.

Table I. Infrared absorption spectra in the region 650-1700 cm^{-1}

$ReO(tu)_4Cl_3.H_2O$ and $ReO(tu)_4Cl_3$	$Re(tu)_3Cl_3$	$[ReO(OH)(tu)_4](ClO_4)Cl.2H_2O$
690 vw	680 w	680 vw
950 s		915 s
		995 m
		1065 sh
		1100 vs
1417 s		1410 s
1515 w	1407 s	
1613 sh	1512 w	1630 sh
1650 vs	1625 vs	1650 vs

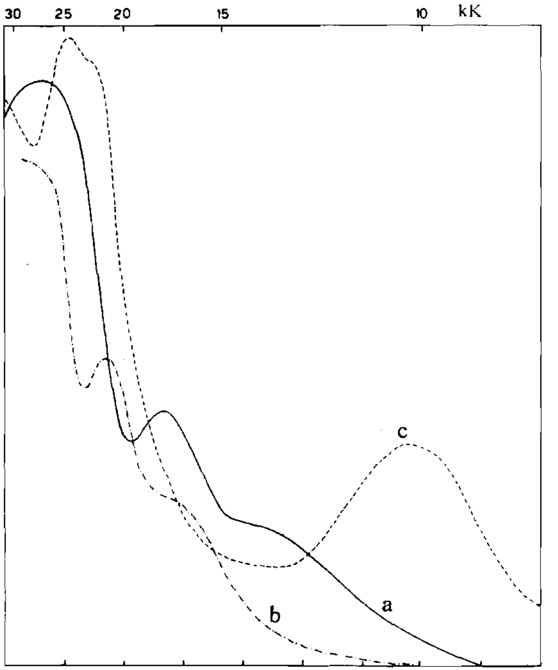

Figure 2. Reflectance spectra of $ReO(tu)_4Cl_3.H_2O$ (a); $ReO_2(tu)_4ClO_4.4H_2O$ (b); $Re(tu)_3Cl_3$ (c).

Chromatograms using 6 N HCl and 3% tu solution as eluent, that is a solution of approximately the same composition as that from which the compound can be precipitated, have shown the complex to be more adsorbed on the cationic ion exchange paper SA-2 (Rf=0.22) than on the anionic SB-2 (Rf=0.45). The difference is even greater in 4 N HCl (3% tu) where Rf values are 0.05 and 0.45 respectively. Since the conductivity of solutions in anhydrous methanol is about twice that of tetramethylammonium chloride solutions of same concentration, the compound can be formulated as $[ReO(tu)_4Cl]Cl_2 . H_2O$.

In solutions of lower tu and HCl concentration the above compound is probably in equilibrium with other species containing different amounts of tu and chloride, in fact a lower chloride content usually characterizes the analysis of compounds obtained from less concentrated hydrochloric acid solutions. In Ref. 9 derivatives with only 3, 2, and 1 tu molecules are mentioned besides the compound $[Re(OH)_2(tu)_4]Cl_3 . 4H_2O$, but no details are given or preparation procedures. The infrared spectrum reported for the above compound appears to be very similar to that we have measured for (I), except for a shift of one band from 950 cm^{-1} to 930 cm^{-1}, which may be due to the different formulation of the two compounds. However we do not agree completely with the assignement of the 1650 cm^{-1} and 1613 cm^{-1} bands, to water of crystallization and to NH_2 bending respectively, since we have observed identical bands both in the hydrated and anhydrous form of our complex. Since similar bands are also found in other anhydrous tu complexes,[16,17] we conclude that tu as well as water may be responsible of the 1650 cm^{-1} band.

A compound approaching the formula $[ReO_2(tu)_4](ClO_4) . 4H_2O$ (II) or $[ReO(OH)(tu)_4](ClO_4)Cl.2H_2O$ (III) is obtained from 4 N HCl solutions by addition of perchloric acid. Its reflectance spectrum is reported in Figure 2b and its I.R. spectrum in Table I.

The presence of perchlorato anions and of water is confirmed by a strong band at 1100 cm^{-1} and by a band at 3550 cm^{-1} respectively. The compound does not show in the I.R. spectrum the single band at about 820 cm^{-1} which is usually assigned to the *trans*-dioxo-rhenium group and two bands at 915 cm^{-1} and 990 cm^{-1} are found instead. These can be explained assuming that the complex contains either a *cis*-dioxo-rhenium group, for which two bands are predicted,[15] or the ReO(OH) group of (III). Experimental evidence is perhaps in favour of the second alternative as the complex $[ReO(OH)en_2](ClO_4)_2$ has similar bands[15] at 980 cm^{-1} and 929 cm^{-1} and since our compound cannot be precipitated from perchloric acid solutions of the reactants, in the absence of hydrochloric acid.

Re^{III}-thiourea Complexes. In a chromatographic and spectrophotometric study of Re and Tc -tu complexes Lederer and Beckmann[3] report that by addition of three equivalents of $SnCl_2$ to a solution containing one mole of NH_4ReO_4 and excess tu a yellow colour and a brown precipitate are produced. We have now analyzed the precipitate and found for it the formula $Re(tu)_3Cl_3$. The reflectance spectrum of the compound

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(Figure 2c) is very similar to that of the yellow solutions, so that it may be argued that they contain a trivalent rather than a tetravalent rhenium complex.

The magnetic moment of the compound is 1.34 B.M. at room temperature, which is similar to that of the known octahedral complexes of rhenium(III).[18,19] The magnetic moment of Re^{IV} complexes, as the hexahalogeno, hexacyano, and hexathiocyanato, is in the range 2.9-3.5 B.M.[20]

The infrared spectrum shows no absorption peaks in the range 700-1000 cm^{-1}, thus confirming the absence of oxygen atoms bound to the metal.[11]

A compound of identical formula and I.R. spectrum is reported by Cotton *et al.*[8] The reflectance spectrum however is significantly different. Due to difficulties encountered at repeating Cotton's preparation, we were unable to study the two compounds comparatively. They may be geometrical isomers, or may have a different degree of polymerization. Our compound behaves electrophoretically as a cation[3] and molecular weight measurements in methanol have indicated a value of about one half that calculated for $Re(tu)_3Cl_3$.

Tc^{III}-thiourea Complexes. Orange solutions are produced by treating any of the following substances TcO_4^-, $TcOCl_5^{2-}$, $TcCl_6^{2-}$ with tu in 2 N HCl or HNO_3.[2,3,7] This led to the conclusion that the complex was a Tc^{IV} derivative. The similarity of the chromatographic, electrophoretic and spectroscopic behaviour of this compound with that of the yellow $Re(tu)_3Cl_3$[3], makes now highly probable that in fact it is an analogous Tc^{III} derivative.

Tc^{V}-thiourea Complexes. The reaction between $TcOCl_5^{2-}$ and tu in 2 N HCl was first studied by Lederer and Roch,[7] who observed the existence of an intermediate product before Tc^{V} was reduced to the orange Tc^{III} complex. We have tried to extend their investigations to elucidate the nature of the compounds by analogy with the Re^{V} complexes. However the instability of the Tc^{V} complexes, which are reduced very rapidly by tu, and technical difficulties due to the limited amount of Tc available and its radioactive nature, seriously hindered our efforts.

By mixing $TcOCl_5^{2-}$ and tu in 6 N HCl a bright yellow colour forms immediately. The spectrum of this solution shows an intense peak at 406 mμ and a much less intense one at 750 mμ. The colour is stable for a few hours, provided the tu concentration does not exceed much that of pertechnetate. On standing for a longer time, the colour fades and the spectrum becomes similar to that measured for $TcCl_6^{2-}$ in 6 N HCl, with an absorption peak at 340 mμ and a shoulder at 308 mμ. In more concentrated tu solutions the colour changes very rapidly to orange even at room temperature.

Analogous yellow solutions are produced very easily with phenylthiourea and sym-diphenylthiourea (λ_{max}= 400 mμ and 406 mμ respectively).

In 2 N HCl solutions of $TcOCl_5^{2-}$ and tu a broad shoulder is found in the spectrum at 380 mμ and only an ill defined shoulder at 406 mμ.

The pale yellow colour of this solution turns also rapidly orange in the presence of excess tu.

The Rf values of the compounds obtained in 6 N HCl or in 2 N HCl, is in any case approximately 0.5 on Whatman No. 1 paper, using either 6 N HCl 2 N HCl as eluent. Re^{V} pink complexes have Rf 0.4 when the eluent is 2-4 N HCl and contains very little or no tu. Whith less concentrated HCl and more tu, they turn pink during the development of the chromatogram. On SA-2 and SB-2 ion exchange papers, strong absorption is observed. It must be pointed out however that to obtain $Rf \neq 0$ for Re complexes on SB-2 paper it is necessary to dissolve 2-3% tu in the eluent and this cannot be done for Tc complexes, since it causes their reduction.

It may be concluded that more than one complex can be formed by Tc^{V} with tu, depending on HCl concentration, in the same way as with Re^{V} complexes, and that they probably do not contain a number of coordinated molecules as great as four, for reduction rather occours under the conditions where this can be achieved for the rhenium complexes.

The yellow colour observed by Lederer and Roch in the reduction of TcO_4^- by diphenylthiourea,[7] was probably due to a Tc^{V} derivative, since the Rf obtained by their chromatograms is in good agreement with that we have measured for the yellow compound that can be obtained from $TcOCl_5^{2-}$ and tu (Rf=0.7 o nWhatman No. 1, HCl as eluent). Moreover we were able to observe the yellow Tc^{V} intermediate also in the reaction of TcO_4^- with tu.

Experimental Section

$ReO(tu)_4Cl_3.H_2O$ and $ReO(tu)_4Cl_3$. 0.57 g of NH_4ReO_4 and 0.30 g of tu were dissolved in 50 ml of 6 N HCl. 0.45 g of $SnCl_2$ in 10 ml of 6 N HCl were slowly added. To the deep blue solution a further amount of tu (about 1 g in the minimum amount of 6 N HCl) was added. The greenish crystalline precipitate was filtered, washed sparingly with 6 N HCl and dried in a vacuum desiccator, over NaOH.

Anal. Found: C, 7,78; H, 2.66; N, 17.71; S, 20.17; Cl, 16.86. Calcd. for $ReO(tu)_4Cl_3.H_2O$: C, 7.61; H, 2.85; N, 17.75; S, 20.28; Cl, 16.85.

The values for C and H analyses are in better agreement with those calculated for $ReO(tu)_4Cl_3$ (see below) but the samples were dried at 110°C before the analyses were performed.

Anal. Calcd. for $ReO(tu)_4Cl_3$: C, 7.83; H, 2.61; N, 18.27; S, 20.88; Cl, 17.35. Found for a sample dried at 80°C: C, 7.71; H, 2.51; N, 18.24; S, 20.73; Cl, 17.18.

$[ReO(OH)(tu)_4](ClO_4)Cl.2H_2O$. This compound was prepared in a manner analogous to that for (I), using solutions which contained 4 N HCl and 2 N $HClO_4$. The precipitate was washed with 6 N HCl.

Anal. Calcd. for $[ReO(OH)(tu)_4](ClO_4)Cl.2H_2O$: C, 6.92; H, 3.02; N, 16.14; S, 18.46; Cl, 10.21.

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(20) B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, 6, 145 (1964).

Calcd. for $[ReO_2(tu)_4](ClO_4) \cdot 4H_2O$: C, 6.92; H, 3.46; N, 16.15; S, 18.47; Cl, 5.11. Found: C, 6.93; H, 3.32; N, 16.00; S, 18.52; Cl, 7.02.

The strong error found in the chlorine content may be explained by the ease by which the compound loses weight by heating. At 60°C the loss is greater than 12% in a few minutes.

Re(tu)$_3$*Cl*$_3$. 1.07 g of NH_4ReO_4 and 1.5 g of tu were dissolved in 60 ml of 2 N HCl. An excess over four equivalents of $SnCl_2$ in 2 N HCl was quickly added, to avoid precipitation of intermediate reduction products. The dark brown solution was left standing for 10-20 minutes, untill brown needles precipitated. The precipitate was filtered, washed with 2 N HCl and dried in vacuo over NaOH.

Anal. Calcd. for $Re(tu)_3Cl_3$: C, 6.92; H, 2,32; N, 16.14; S, 18.47; Cl, 20.41. Found: C, 6.78, 6.76; H, 2.48, 2.05; N, 15.91, 16.07; S, 18.16, 18.40; Cl, 20.13, 20.56.

Visible and ultraviolet spectra were recorded on a Beckman DK-1A recording spectrophotometer, using stoppered silica cells. I.R. spectra were recorded on a Beckman I.R.-7 spectrophotometer, in nujol mulls.

Electrophoresis were performed on a CAMAG high voltage apparatus, with circulating tap water, at about 15°C.

A vapor pressure osmometer Mod. 301 A, of the Mechrolab Inc. was used for molecular weight measurements.

SA-2 and SB-2 ion exchange resin papers were supplied by Rohm and Haas. Chromatograms were obtained with the ascending technique.

Acknowledgments. We wish to thank Dr. Ercolani for the magnetic moment measurements which were obtained with the Gouy method. This work was carried out under the contract N. 365/RB with the International Atomic Energy Agency (Vienna).