With ϵ taken as 2.3 for the benzene solutions and a as 2.5 Å., ΔE is calculated as 0.3 for the 1e,2e molecules and zero for the 1p,2p, which means that the energy difference between the two forms should be about 0.3 greater in benzene solution than in the vapor, as compared to the observed difference 0.2, an agreement as good as could be hoped for with the approximations involved in the calculation. It is evident that the dipole moment values observed for the isomers of 1,2-dichlorocyclohexane are consistent with the existence of the molecules entirely in the chair form, but this fact is not inconsistent with the existence of a tautomeric equilibrium between the chair form and a small amount of the boat form as indicated by thermodynamic evidence.[13]

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Reaction of Osmium Tetroxide with Thiourea

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The red complex formed by the reaction of thiourea with osmium tetroxide in acidic medium contains trivalent osmium and has the composition $[Os(NH_2CSNH_2)_6]^{+++}$ in solution. Osmium in this compound can be reduced to the divalent state with chromous chloride. In the presence of much chloride, yellow-brown mixed chlorothiourea complexes of Os(III) can be formed. $[OsO_2(NH_2CSNH_2)_4]^{++}$ is an intermediate product in the osmium tetroxide–thiourea reaction and can be isolated as the slightly soluble sulfate.

The composition of the soluble red product formed by the reaction of excess thiourea with osmium tetroxide or chloroösmate in acidic medium is uncertain. Chugaev crystallized a red solid from the reaction mixture, which on analysis gave a percentage composition interpretable as corresponding to either $[Os(NH_2CSNH_2)_6]Cl_3{\cdot}H_2O$ or $[Os(NH_2CSNH_2)_6]OHCl_3$. In his early paper on the subject, Chugaev[2] accepted the first formula, but later[3] rejected it in favor of the second formula, thus assigning osmium a valency of +4 in the complex. Sidgwick[4] accepts the quadrivalency of osmium in the compound, but writes the formula as $[Os(NH_2CSNH_2)_6]Cl_4{\cdot}4H_2O$, apparently without new experimental evidence.

We have established the composition of the red compound in solution by obtaining the valency of osmium and the osmium–thiourea ratio. The complex is found to be the hexathioureaosmium(III) cation. In the course of this work a thiourea complex of hexavalent osmium was prepared, and observations were made on the reaction of thiourea with Os(VIII) and Os(IV) at high chloride concentrations.

Experimental

Apparatus and Materials.—A Beckman model B spectrophotometer with 1-cm. Pyrex cells was used for absorbance measurements.

Solutions of osmium tetroxide were standardized by the Klobbie iodometric method with starch as external indicator. Thiourea (Eastman Kodak Co., white label) was recrystallized from water. Chromous chloride solution was prepared and standardized by customary methods.

Valence of Osmium in the Red Complex.—This was obtained by potentiometric titration with chromous chloride. Five ml. of 0.0154 M osmium tetroxide solution was treated with 5 ml. of concentrated hydrochloric acid and 5 ml. of 2% thiourea solution in a titration cell. Oxygen was removed by bubbling nitrogen through the solution and the titration was made with 0.0508 M chromous chloride solution. Both a platinum and a mercury electrode were used as indicator electrodes. After addition of 7.65 ml. of chromous chloride, both electrodes showed a sharp break in potential (Fig. 1), but the solution retained its intense red color. Further addition of chromous chloride resulted in another break (mercury electrode) at 9.20 ml. total, at which the red color disappeared. The two breaks in this, and replicate, titrations, correspond to the following ratios of moles Cr(II) oxidized to moles Os present: first, 5.05, 4.95, 5.02; second, 6.07, 5.98, 6.03.

In the next series of experiments, a solution of the red complex formed as before was reduced with an excess of chromous chloride and air was then bubbled through for 20 minutes to oxidize all Cr(II) and restore osmium to its original valence in the red complex. After removal of oxygen, the solution was titrated with chromous chloride. The end-point in duplicate titrations, with the mercury electrode as indicator electrode, corresponded to the addition of 0.995 and 1.010 moles of Cr(II) per mole of osmium present.

Ratio of Thiourea to Osmium in the Red Complex.—Constant amounts of osmium tetroxide at a final concentration of 1.01×10^{-4} M in 0.25 M sulfuric acid were treated with varying amounts of thiourea and the transmittancy of the solutions was determined at 480 mμ after attainment of constant readings, which for low ratios of thiourea to osmium required an hour. The data are shown in Fig. 2.

Reaction of Thiourea with Osmium Tetroxide in the Presence of Much Chloride.—Thiourea was added to acidified osmium tetroxide solutions in the molar ratio 11.14:1 (approximately 1% in excess of the amount required to form the red complex) in the presence of various amounts of chloride. After 24 hours standing, when at least an approach to equilibrium had been attained, the absorbance curves recorded in Fig. 3 were obtained. No attempt was made to isolate a solid phase.

Preparation and Analysis of Tetrathioureadioxoösmium (VI) Sulfate.—Five ml. of 5% thiourea solution was added to 25 ml. of 0.015 M osmium tetroxide solution in 0.3 M sulfuric acid. The brown precipitate soon forming was filtered off, washed with 0.01 M sulfuric acid and finally with small portions of cold water. The crystalline product was dried at room temperature over anhydrous magnesium perchlorate. The yield was 80%.

Analysis of the compound was carried out as follows: osmium by dissolving in a dilute sulfuric acid solution of thiourea and measuring the optical density of the red solution; sulfate by dissolving in dilute hydrochloric acid, and precipitating and weighing as barium sulfate; thiourea by determination of nitrogen by the Dumas method, and also from the total sulfur content found after decomposing the sample with concentrated nitric acid. These analyses were made on the semi-micro scale. The percentage composition

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(1) From the Ph.D. thesis of R. D. Sauerbrunn, 1952.

(2) L. A. Chugaev, *Bull. soc. chim.*, **23**, 377 (1918); *Compt. rend.*, **167**, 235 (1918).

(3) L. A. Chugaev, *Z. anorg. allgem. Chem.*, **145**, 65 (1925).

(4) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, 1950, p. 1495.

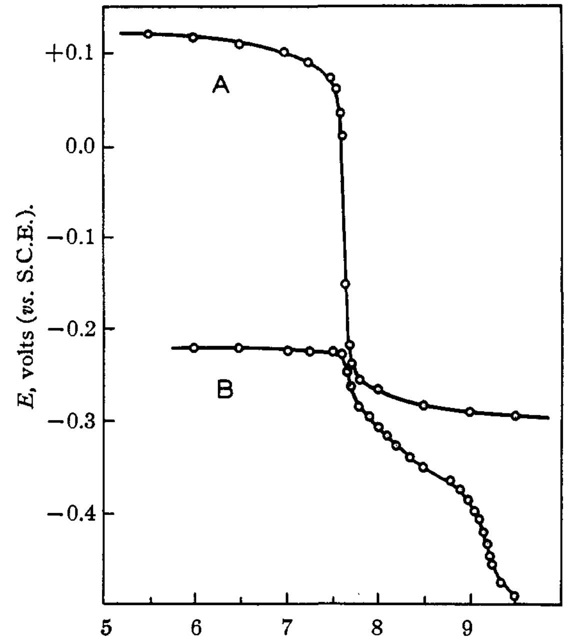


Fig. 1.—Potentiometric titration of a mixture of OsO_4 and excess thiourea with chromous chloride solution: A, Pt electrode; B, Hg electrode.

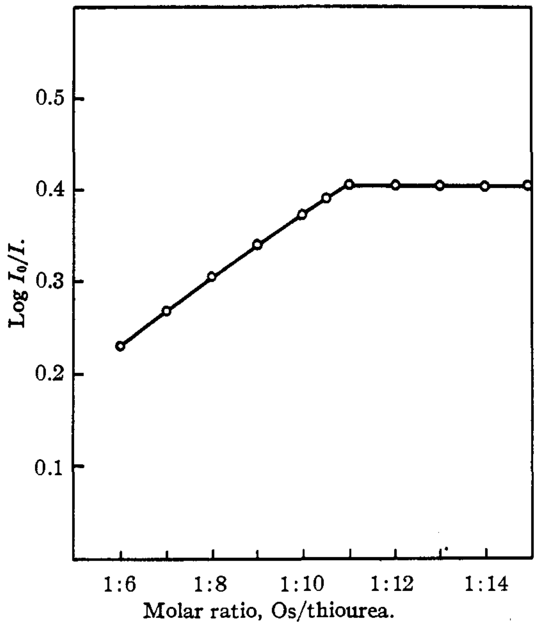


Fig. 2.—Absorbance of 1.01 × 10^{-4} M OsO_4 with various amounts of thiourea (480 mμ, 1-cm. cell).

found and the calculated composition for $OsO_2(NH_2CSNH_2)_4SO_4$ are

	Calculated	Found	Molar ratios
Os	30.54	30.5	1.00
NH_2CSNH_2	48.90	47.0 (from total S) 49.9 (from N)	3.97
SO_4	15.43	15.9	1.03

Potentiometric titration of a solution of the compound in 2 *M* hydrochloric acid with chromous chloride (reduction to trivalent osmium) required 2.95 equivalents of Cr(II) per mole of Os, thus showing osmium to have a valence of +6.

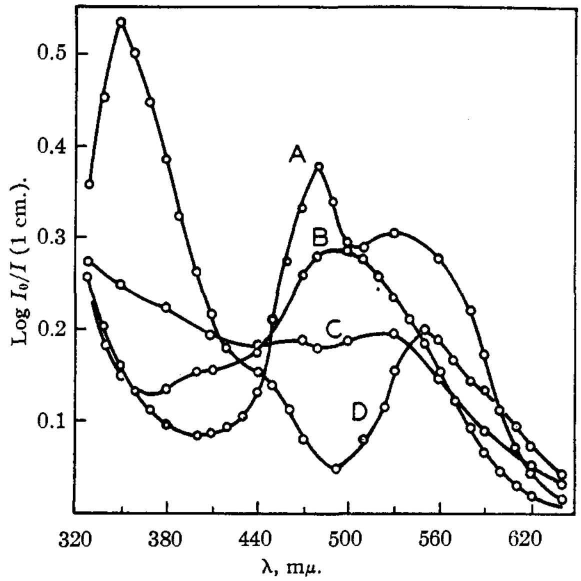
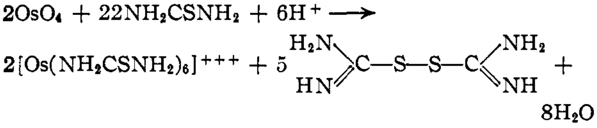


Fig. 3.—Absorbance curves of 9.7 × 10^{-5} M Os(III)—1.1 × $10^{-3}M$ thiourea—Cl^-: A, no Cl^-, 1.0 M H_2SO_4; B, 2.1 M HCl; C, 5.4 M Cl^- (2.1 M HCl, 3.3 M LiCl); D, 9.6 M Cl^- (2.1 M HCl, 7.5 M LiCl).

Discussion

The data obtained show that in solution the composition of the red compound formed when osmium tetroxide reacts with excess thiourea in acidic medium is $[Os(NH_2CSNH_2)_6]^{+++}$. The reaction takes place according to the equation



$$2OsO_4 + 22NH_2CSNH_2 + 6H^+ \longrightarrow 2[Os(NH_2CSNH_2)_6]^{+++} + 5\,(H_2N)(HN{=})C{-}S{-}S{-}C({=}NH)(NH_2) + 8H_2O$$

Oxidizing agents in acidic solution are known to convert thiourea into formamidine disulfide; the latter can be converted back to thiourea by strong reducing agents.[5] Accordingly when osmium tetroxide is treated with excess thiourea and the solution is titrated with chromous chloride, the first end-point marks the completion of the reduction of formamidine disulfide to thiourea. Since at the first end-point 5 equivalents of chromous chloride have been consumed per mole of osmium, the valency of osmium in the red complex must be +3. As the titration is continued, reduction of Os(III) in the complex takes place, the red color disappears, and the second end-point is reached after another equivalent to Cr(II) has been added and osmium is wholly in the divalent state. This one-electron change is verified by converting formamidine disulfide into thiourea by adding excess chromous chloride, oxidizing the latter and Os(II) with oxygen, and titrating with chromous chloride.

It is to be noted that the chromous reduction of chloroösmate, $OsCl_6^=$, or of osmium tetroxide in hydrochloric acid solution, proceeds only to trivalent osmium ($OsCl_6^{\equiv}$ or a similar ion).[6] The reduction of $[Os(NH_2CSNH_2)_6]^{+++}$ to Os(II) in

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(5) E. A. Werner, *J. Chem. Soc.*, **101**, 2168 (1912).

(6) W. R. Crowell and H. L. Baumbach, THIS JOURNAL, **57**, 2607 (1935). Their observations are in accord with ours.

the presence of excess thiourea is analogous to the behavior of the dipyridyl[7] and *o*-phenanthroline[8] cation complexes of trivalent osmium, which also show the reversible oxidation–reduction Os(III) $\rightleftarrows$ Os(II).

From the break at the molar ratio 11 thiourea:1 osmium in Fig. 2 it is evident that this ratio in the complex is 6, the remainder of the thiourea having been consumed in the reduction of Os(VIII) to Os(III). Migration experiments showed that the red species moves toward the cathode. Therefore in solution the red complex is the cation $[Os(NH_2CSNH_2)_6]^{+++}$.

The upward sloping line on the left in Fig. 2 represents the absorbance of mixtures of $[Os(NH_2CSNH_2)_6]^{+++}$ and brown $Os(OH)_4$, most of the latter doubtless being present in colloidal solution; migration experiments showed the brown component to be uncharged. A series of absorbance curves (not reproduced here) for osmium–thiourea ratios ranging from 1:6 to 1:15 showed an isosbestic point at 440 mμ, thus indicating the presence of only two components in the solution. No evidence has been obtained for the existence in sulfuric or perchloric acid solutions of appreciable amounts of any osmium(III)–thiourea complex other than the hexathiourea compound.

High acidities (*e.g.*, 6 *N* perchloric or sulfuric acid) do not inhibit the formation of the red complex, in agreement with expectations based on its nature. In this respect Os(III) differs markedly from Ru(III), which forms the chelate complexes, $[Ru(NHCSNH_2)]^{++}$ and $Ru(NHCSNH_2)_3$, and whose reaction with thiourea is therefore strongly dependent on hydrogen ion concentration.[9]

Osmium–Thiourea Reaction in Presence of Chloride.—When the ratio of chloride to thiourea is very high, mixed chlorothiourea complexes can be formed. This is demonstrated by Fig. 3, where the curves represent the absorbance of systems obtained by adding much chloride to $[Os(NH_2CSNH_2)_6]^{+++}$ with a very slight excess of thiourea present. The mixed complexes are yellow to brown in color and more than one is formed. They move toward the cathode on electrolysis. These cations may be $[Os(NH_2CSNH_2)_5Cl]^{++}$ and $[Os(NH_2CSNH_2)_4Cl_2]^{+}$, the iridium[10] and rhodium[11] analogs of which have been prepared as salts. The mixed complexes were not studied further because of the extreme slowness of attainment of equilibrium at room temperature. At higher temperatures hydrolysis of thiourea takes place.

In contrast to the rapid reaction between thiourea and osmium tetroxide, the reaction between thiourea and $OsCl_6^{=}$ is exceedingly slow at room temperature. Even at 100°, with a large excess of thiourea (0.05 *M*) in the mixture approximately one-half hour is required for quantitative conversion of chloroösmate into $[Os(NH_2CSNH_2)_6]^{+++}$ in 1 *M* hydrochloric acid medium. The addition of stannous chloride, which reduces Os(IV) to Os(III), shortens the reaction time by about one-half. With the concentrations of hydrochloric acid and thiourea mentioned practically all of the osmium is eventually transformed into the red complex and the concentration of the mixed chlorothiourea complexes is very small.

Tetrathioureadioxoösmium(VI) Sulfate.—As might be expected, the reduction of Os(VIII) by thiourea proceeds through the osmyl stage. When acidified solutions of osmium tetroxide not too dilute (*e.g.*, 0.01 *M*) are treated with thiourea, a yellow to brown coloration first appears, but rapidly gives way to the red of $[Os(NH_2CSNH_2)_6]^{+++}$. The transient brownish color is due to $[OsO_2(NH_2CSNH_2)_4]^{++}$. If sulfate is present in the solution and the excess of thiourea is restricted, the slightly soluble salt $OsO_2(NH_2CSNH_2)_4SO_4$ can be isolated. This complex is the analog of the ammine $OsO_2(NH_3)_4X_2$ (X = Cl, $^1/_2$ SO_4, $^1/_2$ C_2O_4) prepared by Gibbs.[12]

Tetrathioureadioxoösmium(VI) sulfate dissolves in acidic thiourea solutions to give $[Os(NH_2CSNH_2)_6]^{+++}$. In water or dilute acid solutions it is decomposed to give brown colloidal $Os(OH)_4$ as the main product, which no longer reacts with thiourea.

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[7] F. H. Burstall, F. P. Dwyer and E. C. Gyarfas, *J. Chem. Soc.*, 953 (1950).

[8] F. P. Dwyer, N. A. Gibson and E. C. Gyarfas, *J. Proc. Royal Soc. New South Wales*, **84**, 68 (1950).

[9] R. P. Yaffe and A. F. Voigt, THIS JOURNAL, **74**, 2503 (1952).

[10] V. V. Lebedinskii, E. S. Shapiro and N. S. Kasatkina, *Ann. inst. platine*, No. **12**, 93 (1935).

[11] V. V. Lebedinskii and V. S. Volkov, *ibid.*, No. **12**, 79 (1935).

[12] W. Gibbs, *Am. Chem. J.*, **3**, 238 (1881).