TABLE I

SPECTRAL DATA FOR REDUCED 2:18 ANIONS IN THE VISIBLE AND NEAR-INFRARED SPECTRA

Anion	Position[a] (intensity[b]) of maxima
$H_2P_2Mo_{18}O_{62}^{6-}$	13.2 (11,000), 9.0 sh[c] (4600)
$H_4P_2Mo_{18}O_{62}^{6-}$	14.8 (19,400), 11.2 sh (12,000)
$H_6P_2Mo_{18}O_{62}^{6-}$	16.7 (27,600), 14.5 sh (23,800)
A-$P_2W_{18}O_{62}^{7-}$	13.3 (6000), 11.2 (5400)
A-$P_2W_{18}O_{62}^{8-}$	14.1 (13,100), 11.3 sh (6200)
A-$H_2P_2W_{18}O_{62}^{8-}$	15.4 (25,800), 9.5 (13,000)
A-$H_4P_2W_{18}O_{62}^{8-}$	28.0 (13,000), 16.5 (23,000), 11.2 (13,000)
B-$P_2W_{18}O_{62}^{7-}$	14.0 sh (3600), 11.0 (4400)
B-$P_2W_{18}O_{62}^{8-}$	14.4 (10,600), 10.7 sh (6600)
B-$H_2P_2W_{18}O_{62}^{8-}$	16.0 (23,300), 10.2 sh (12,200)
B-$H_4P_2W_{18}O_{62}^{8-}$	29.0 (9500), 17.1 (23,800), 10.8 sh (9100)

[a] kK; uncertainty ±0.2 kK. [b] Molar absorptivity, ±100 l. mol^{-1} cm^{-1}. [c] Shoulder.

six-electron blues of the tungstophosphates is not paralleled in the spectrum of the corresponding molybdophosphate. We suggest that this change reflects a transition to a more delocalized (class III-A) structure for the former species.[8] An analogous transition (semiconductor to metal) has been noted with the tungsten bronzes M_xWO_3 and seems to occur at x = *ca.* 0.25 for both these materials[9,10] and the related species $WO_{3-x}F_x$ and $W_{1-x}Re_xO_3$.[11] For the bronzes, where the transition metal cations are quite widely separated (*ca.* 5.4 Å), the evidence seems to be in favor of a conduction band formed through overlap of the t_{2g} orbitals of the tungsten (rhenium) atoms with the appropriate p orbitals of the oxygens.[12] According to this model, distortions of the WO_6 octahedra occur at low x values leading to a permanent electric moment and the quenching of metallic conduction. In the heteropolytungstates the tungsten atoms are closer together (*ca.* 3.4 Å) than in the bronzes and it would seem that "delocalization" of the electrons could occur through direct metal–metal orbital overlap, when the concentration of added electrons is sufficiently great. An analogous model had once been favored for the bronzes.[13]

According to its spectrum no analogous transition has occurred in the six-electron blue of $P_2Mo_{18}O_{62}^{6-}$, which is isostructural with the B isomer of the tungstate.[14] It is to be expected, in view of the smaller size of the 4d compared with the 5d orbitals, that transition to a class III-A species would require a higher concentration of added electrons in a polymolybdate than in an isostructural polytungstate. In support of such an argument applied to the bronzes, it may be noted that the molybdenum bronzes M_xMoO_3 become metallic only when x exceeds *ca.* 0.5. Thus $Rb_{0.27}MoO_3$ and $Rb_{0.41-0.44}MoO_3$ are both semiconductors while $K_{\sim 0.5}$-MoO_3 is metallic.[15]

(8) An atomic structural rearrangement is unlikely in view of the fact that the blue solutions can be rapidly reoxidized without isomerization occurring, thus demonstrating the inertness of the polytungstate networks.

(9) M. J. Sienko and T. B. N. Truong, *J. Am. Chem. Soc.*, **83**, 3939 (1961).

(10) In this connection we may note that the reflectance spectra of tungsten bronzes are formally similar to those reported here in that the former show a broad absorption band which undergoes a hypsochromic shift as x increases: B. W. Brown and E. Banks, *ibid.*, **76**, 963 (1954).

(11) A. W. Sleight, *Inorg. Chem.*, **8**, 1764 (1969).

(12) J. B. Goodenough, *Bull. Soc. Chim. France*, 1200 (1965).

(13) M. J. Sienko in "Nonstoichiometric Compounds," Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p 224.

(14) Early optical crystallography indicates that the following salts [modern formulation] are isomorphous: B-$(NH_4)_6[P_2W_{18}O_{62}]\cdot 14H_2O$, B-$K_6[P_2W_{18}O_{62}]\cdot 14H_2O$, $K_6[P_2Mo_{18}O_{62}]\cdot 14H_2O$, and $(NH_4)_6[As_2W_{18}O_{62}]\cdot 14H_2O$: L. Duparc and F. Pearce, *Bull. Soc. Franc. Mineral.*, **18**, 31 (1895); *Z. Kryst.*, **27**, 612 (1897); **31**, 66 (1899).

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Synthesis of Hexakis(thiourea)ruthenium(III)

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The reaction of ruthenium(III) with thiourea to form complex ions is of analytical importance, and much work has been done toward developing a reliable, albeit empirical, method of analysis.[1] This empirical nature inspired a theoretical study of the reaction by Yaffe and Voigt,[2] who concluded that only two complexes were present in a perchloric acid solution containing Ru(III) and thiourea. These were $RuTu^{2+}$ and $RuTu_3$. To satisfy secondary and primary valency requirements four-membered chelate rings were postulated. The thiourea was assumed to react as an acid, and evidence was presented that hydrogen ion concentration enters directly into the reaction equilibrium.

Yamaguchi and coworkers[3] studied the infrared spectra of thiourea and thiourea complexes of Pt(II) and Pd(II). They concluded that sulfur to metal bonds are found in the compounds $PtTu_2Cl_2$ and $PdTu_2Cl_2$. Valency considerations require the thiourea ligands to be neutral in these compounds.

Lebedenskii and coworkers[4,5] prepared a series of iridium and rhodium compounds in which three, four, five, or six thiourea molecules replaced a like number of chloride ions in the metal hexachlorides. Compounds containing one or two thiourea ligands could not be precipitated. The experiments indicated, however, that the reaction of thiourea with rhodium and iridium occurs in steps and any reaction solution would contain a mixture of compounds.

(1) G. H. Ayres and F. Young, *Anal. Chem.*, **22**, 1277 (1950).

(2) R. P. Yaffe and A. F. Voigt, *J. Am. Chem. Soc.*, **74**, 2503 (1952).

(3) A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran, and J. V. Quagliano, *ibid.*, **80**, 527 (1958).

(4) V. V. Lebedenskii and V. S. Voldor, *Ann. Inst. Platine* (U.S.S.R.), **12**, 79 (1935).

(5) V. V. Lebedenskii, E. S. Shipiro, and N. P. Kasatkins, *ibid.*, **12**, 93 (1935).

Osmium(III) is known to form $OsTu_6^{3+}$. No crystallization of a ruthenium–thiourea complex has been reported, but one would expect thiourea to displace chloride in $RuCl_6^{3-}$ in a manner analogous to the $OsCl_6^{3-}$, $RhCl_6^{3-}$, and $IrCl_6^{3-}$ displacements. This paper reports the preparation of $RuTu_6^{3+}$ by such a displacement.

Results and Discussion

Lebedenskii and coworkers[4,5] described the reaction of thiourea with iridium as capricious and warned of the difficulty in repeating their syntheses. The compound $IrTu_6Cl_3$ was readily prepared, although yields were low, 15% on the average.

Several attempts to prepare ruthenium complexes in a way analogous to the rhodium and iridium methods failed.[6] For instance, the green ruthenium complex would not precipitate under conditions used for the precipitation of $IrTu_6Cl_3$. By adding isopropyl alcohol to aqueous solutions it was possible to separate the complex from most of the solvent; efforts at further purification, however, resulted in decomposition of the product. Thus the stratagem of adding the heavy anion HgI_4^{2-} was adopted as a means of obtaining a crystalline complex of ruthenium and thiourea. The anion does not absorb in the infrared spectrum between 2 and 15 μ and hence is useful for studying frequency shifts of the complexed thiourea molecule and for determining the maximum number of ligands in the ruthenium complex cation.

In evaluating their work with the spectra of thiourea and its complexes with Pt and Pd, Yamaguchi, *et al.*,[3] concluded that the most significant changes are observed in the 1100- and 700-cm^{-1} regions. The strong absorption band at 1083 cm^{-1} is greatly reduced or eliminated when thiourea is complexed with Pt and Pd. This is explained as due to considerable change in the nature of the N—C bond and the C═S bond on coordination of thiourea through the sulfur atom; the N—C—N stretching frequency is increased and the C═S stretching frequency is decreased. However, since the symmetric N—C—N stretching vibration cannot contribute much to the band intensity, the result is a decrease in intensity and a shift in frequency because of reduced double-bond character of C═S. The lowering of frequency in the 700-cm^{-1} region is also attributed to reduced double-bond character of C═S. Bellamy[7] also assigned C═S bonds to these regions. Bands at about 1400 cm^{-1} are assigned to NH_2 rocking vibrations and N—C—N and C═S stretching vibrations; these are changed slightly by complexation. In the 1500-cm^{-1} region, increased frequency is attributed to increased carbon-to-nitrogen double-bond character, as N–C–N stretching vibration is assigned to this region. The bands at 1600 cm^{-1} are assigned to the NH_2 bending vibrations; these are little changed by complexation. Lastly, the bands around 3300 cm^{-1} are assigned to N–H stretching vibrations; the increased sharpness of the bands in the complexes suggests that hydrogen bonding is not present. All of the above spectral changes are similarly observed with the thiourea complexes of rhodium, iridium, ruthenium, platinum, and palladium (Table I). Thus one may conclude that bonding is from sulfur to metal in all of these complexes.

(6) H. L. Youmans, Ph.D. Dissertation, Louisiana State University, 1961.

(7) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958.

TABLE I
ABSORPTION MAXIMA (CM^{-1}) OF THIOUREA AND HEXAKIS(THIOUREA)RUTHENIUM(III) TETRAIODOMERCURATE(II)

Type of vibration based on calculations of Yamaguchi, *et al.*[3]	Obsd freq: Thiourea	Obsd freq: $[RuTu_6]_2[HgI_4]_3$
N—H str	3390[a]	
	3226	3226
	3077[a]	
NH_2 bend	1610	1610
N—C—N str, B_1 type	1470	1515
NH_2 rock and N—C—N and C═S	1417[b]	1417
str, A_1 type	1076[c]	1101
C═S str, A_1 type	729	685

[a] Present as shoulders in spectrum of complex. [b] Peak band width reduced in complex. [c] Intensity greatly reduced in complex.

Cotton and Wilkinson[8] stated that octahedral Ru(III) complexes have magnetic moments in the range 1.8–2.1 BM at room temperature. Ru(II) complexes are diamagnetic. Ruthenium in $[RuTu_6]_2[HgI_4]_3$ showed magnetic moments of 2.0 ± 0.1 BM.

Adsorption on cationic resins, migration to the cathode in electrodialysis cells, and precipitation by HgI_4^{2-} reveal the cationic nature of the hexathiourea complex of Ru(III).

Table II gives the results of a commercial microanalysis of $[RuTu_6]_2[HgI_4]_3$ compared with the theoretical values for the compound and for $[RuTu][HgI_4]$. The latter compound would be expected from the complex cation of Yaffe and Voigt.

TABLE II

	Ru	C	H	N	S	Hg	I
			$(RuTu_6)_2(HgI_4)_3$				
% calcd	6.3	4.4	1.5	10.3	11.8	18.6	47.0
% found	6.0	4.9	1.5	9.8	11.7	17.2	48.6
			$(RuTu)(HgI_4)$				
% calcd	11.5	1.4	0.5	3.2	3.6	22.5	57.2

Experimental Section

Preparation of Compounds.—Thiourea used in the synthesis of complexes was recrystallized from aqueous solution. Analytical grade thiourea was contaminated with thiocyanate. The impurity was more apparent in the complexes than in the thiourea powder if the thiourea were not recrystallized. $[RuTu_6]_2[HgI_4]_3$ was prepared by dissolving 0.5 g of $RuCl_3$ in 30 ml of 0.3 *N* HCl and adding 3 g of thiourea. The solution was mixed, heated for 10 min on a steam plate, and then cooled in an ice bath. A solution composed of 17 g of KI and 4 g of $HgCl_2$ in 30 ml of 0.3 *N* HCl was added with stirring. The solution was immediately filtered, and the precipitate was washed three times with small portions of 0.3 *N* HCl. Washing was limited because of instability of the precipitate. Recrystallization was

(8) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1962.

impossible. The air-dried precipitate was greenish black and weighed 1.8 g, a yield of 55%.

Absorption Measurements.—The infrared spectra were recorded with a Perkin-Elmer Model 9 spectrophotometer using sodium chloride prisms. KBr disks were used.

Magnetic Moment Measurements.—Magnetic susceptibilities were measured at 27 ± 1° by the Gouy method. Solid Hg[Co(NCS)$_4$] was used to calibrate the instrument. [RuTu$_6$]$_2$[HgI$_4$]$_3$ is paramagnetic and μ_{eff} (with diamagnetic correction of 1306 × 10^{-6} cgsu applied to χ_M of 296 × 10^{-6} cgsu) is 2.0 ± 0.1 BM.

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Dimerization Reactions and Monosubstituted Derivatives of Ruthenium Tetracarbonyl Dihalides

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Ruthenium tetracarbonyl dihalides, Ru(CO)$_4$X$_2$, were isolated by Calderazzo and L'Eplattenier by the reaction of ruthenium pentacarbonyl with halogens.[1] Corey, *et al.*, prepared the diiodide.[2] Cotton, *et al.*, isolated the dibromide and diiodide from the reaction of H$_2$Ru(CO)$_4$ with the appropriate halogen.[3] Johnson, *et al.*, have described an alternative route which involves the action of halogens on Ru$_3$(CO)$_{12}$.[4,5]

We have reconsidered the thermal decomposition of Ru(CO)$_4$X$_2$ (X = Br, I) whereby the corresponding ruthenium tricarbonyl dihalides, [Ru(CO)$_3$X$_2$]$_2$, are obtained

$$2\text{Ru(CO)}_4\text{X}_2 \longrightarrow [\text{Ru(CO)}_3\text{X}_2]_2 + 2\text{CO} \qquad (1)$$

In this paper we shall report a kinetic study of reaction 1 along with a detailed investigation of it under preparative conditions. We have now also found that under relatively mild conditions ruthenium tetracarbonyl halides give monosubstituted products by reaction with pyridine or pyridine derivatives (L)

$$\text{Ru(CO)}_4\text{X}_2 + \text{L} \longrightarrow \text{Ru(CO)}_3\text{X}_2\text{L} + \text{CO} \qquad (2)$$

These novel tricarbonyl derivatives will also be described in this paper.

Results and Discussion

(A) Dimerization Reactions of Ru(CO)$_4$X$_2$.—Reaction 1 proceeds under relatively mild conditions, in such solvents as chloroform. The halogen-bridged complexes have been isolated in only one of the possible isomeric forms as yellow crystals which are stable in solution even in the presence of air. They are diamagnetic in the solid and nonconducting in nitrobenzene solution. These compounds are dimeric: their molecular weights were determined either by osmometric methods or by the appearance of the parent molecular ions in the mass spectra. These compounds have also been isolated by the reaction of Ru$_3$(CO)$_{12}$ and the halogens[4,5] or CHX$_3$.[6,7] The infrared spectra of our compounds in the carbonyl stretching region consist of two strong bands (Table I); the lower one is broader than the upper one and exhibits a shoulder. Such spectral features suggest a C_{2h} symmetry. It should be noted that such shoulder cannot be attributed to the presence of other isomers of these compounds since it would then be accompanied by additional bands, and, more important, it does not correspond to any of the bands observed by other authors and assigned to isomers.[4-7] We feel that this shoulder is probably due to a better resolution resulting from the greater purity of our samples. The infrared evidence does not allow one to distinguish between the two possible isomers, I and II (Figure 1).

TABLE I

CARBONYL STRETCHING FREQUENCIES OF RUTHENIUM CARBONYL DERIVATIVES IN CHCl$_3$ SOLUTION[a]

Compound	ν_{CO}, cm^{-1}				
Ru(CO)$_4$Br$_2$[b]	2177 m	2123 vs	2105 s	2073 s	
Ru(CO)$_4$I$_2$[b]	2160 m	2119 vw	2105 vs	2095 s	2066 s
[Ru(CO)$_3$Br$_2$]$_2$		2131 vs	2065 vs	2059 sh	
[Ru(CO)$_3$I$_2$]$_2$		2122 vs	2064 vs	2050 sh	
Ru(CO)$_3$Br$_2$(C$_5$H$_5$N)		2128 vs	2069 vs	2045 vs	
Ru(CO)$_3$Br$_2$(3-pic)		2138 vs	2078 vs	2052 vs	
Ru(CO)$_3$Br$_2$(3,4-lut)		2138 vs	2078 vs	2052 vs	
Ru(CO)$_3$I$_2$(C$_5$H$_5$N)		2119 vs	2063 vs	2043 s	

[a] All spectra recorded on a Perkin-Elmer Model 621 spectrophotometer. Abbreviations: vs, very strong; s, strong; m, medium; vw, very weak; sh, shoulder. [b] From ref 1.

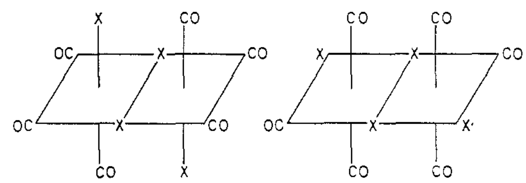

Figure 1.

Thus, we are inclined to assume structure I for our halogen-bridged complexes, similar to that of the compound [Ru(CO)$_3$Br$_2$]$_2$ recently investigated.[8]

(B) Monosubstituted Derivatives of Ruthenium Tetracarbonyl Dihalides, Ru(CO)$_3$X$_2$L (X = Br, I).—Disubstituted derivatives of ruthenium tetracarbonyl dihalides, Ru(CO)$_2$X$_2$L$_2$, are well known and can be

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