rotation about the metal–sulfur bond. The n.m.r. spectrum of the red isomer, however, showed no change at 75°. After heating to 125°, the spectrum was run at 100°, at which temperature it most resembled that of the yellow isomer. Upon evaporation of the chloroform solvent, yellow crystals were obtained whose X-ray powder pattern and melting point were identical with that of the yellow isomer. It is apparent that the isomerization *trans*-$[Ir((C_2H_5)_2S)_4Cl_2]$-*trans*-$[Ir((C_2H_5)_2S)_2Cl_4] \rightarrow$ *cis*-$[Ir((C_2H_5)_2S)_3Cl_3]$ has occurred at elevated temperatures. This reaction appears similar to the conversion of $[Pt((CH_3)_2S)_4][PtCl_4]$ to the monomer $[Pt((CH_3)_2S)_2Cl_2]$.[44] It is interesting to note that in the present case only the *cis* isomer was obtained upon isomerization. Preferential formation of the *cis* isomer over the *trans* isomer may be due to stronger iridium–sulfur π-bonding in the *cis* isomer as suggested for the dichlorobis-(trialkylphosphine)-platinum(II) complexes.[45]

In view of the agreement between the results of the different approaches described in this paper, the authors feel that the structures of the yellow and red isomers of empirical formula $Ir((C_2H_5)_2S)_3Cl_3$ have been definitely established.[46] However, there is need for similar stereochemical investigations of other isomer pairs, especially those of type MA_3B_3, for which configurational assignments have been made on the basis of meager data. Although the configurations finally established in the present case differ from those originally predicted by us on the basis of chromatographic behavior the general rule that the more polar compound should be adsorbed more strongly by polar adsorbents than the less polar compound[4] is still valid. Since it was the discrepancy in elution order which led us to undertake this stereochemical study, the value of chromatographic behavior as a diagnostic tool in structure proof is thus underscored.

Acknowledgment.—In addition to the organizations and individuals acknowledged above, the authors wish to thank Dr. Max T. Rogers of Michigan State University, Drs. T. S. Piper and T. L. Brown of the University of Illinois, and Drs. Robert M. Kallo, Richard P. Ciula, and Roger G. Gymer of Fresno State College for helpful advice. They are also indebted to Dr. A. W. Cordes of the University of Arkansas for attempts to measure dielectric constants for the red isomer in nitrobenzene.

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[44] E. G. Cox, H. Saenger, and W. Wardlaw, *J. Chem. Soc.*, 182 (1934).

[45] J. Chatt and R. G. Wilkins, *ibid.*, 273 (1952).

[46] The preparation of a third isomer has been claimed by Fritsman and Krinitskiĭ (*cf.* ref. 29), but no details or properties are given. This compound may be the true *trans* monomer.

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On the Existence of Red Tungsten(III) and of Pentapotassium Tetradecachlorotritungstate(III) during the Reduction of Chlorotungstates with Tin

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Received May 29, 1963

Comparison of X-ray diffraction data indicates that the substance $K_5[W_3Cl_{14}]$ as reported by Laudise and Young is presumably a mixture of $K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$ instead. This is strongly supported by the changes in absorption spectra observed during the decomposition of $K_2[W(OH)Cl_5]$ solutions. The wine-red color of these solutions is caused by superposition of the absorption spectra of $K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$. The same seems to apply to the red color observed during the reduction of chlorotungstates with tin, which has been attributed to a red tungsten(III) compound. Absorption and reflection spectra of both $K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$ are presented.

Tungstates(VI) when dissolved in 12 *M* hydrochloric acid are at first reduced electrochemically or chemically to a blue solution, which according to oximetric and coulometric measurements[2] contains tungsten(V). The absorption spectrum shows one band at 15,300 cm.$^{-1}$ with $\epsilon \sim 7$ presumably due to the presence of the monomeric species $[WOCl_5]^{2-}$.[3] One single spectral transition is indeed expected in the visible for the $(5d)^1$ system of tungsten(V) in an approximately cubic field of ligands. The appearance of the $[WOCl_5]^{2-}$ ion is supported by the fact that tungsten(V) oxychlorides have been crystallized from solutions reduced to the oxidation state +5 at a platinum cathode.[4]

Continued reduction produces intensely violet colored solutions, an absorption band at 19,100 cm.$^{-1}$ with $\epsilon \sim 600$ having been found by Jørgensen.[3] From these solutions a red compound has been obtained,[5] which has the apparent composition $K_2[W^{IV}(OH)Cl_5]$, whereas it was demonstrated distinctly by means of

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[2] J. J. Lingane and L. A. Small, *J. Am. Chem. Soc.*, **71**, 973 (1949).

[3] C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 73 (1957).

[4] (a) O. Collenberg and J. Backer, *Z. Elektrochem.*, **30**, 230 (1924); (b) O. Collenberg and A. Guthe, *Z. anorg. allgem. Chem.*, **134**, 322 (1924).

[5] O. Olsson, *Chem. Ber.*, **46**, 566 (1913).

polarographic investigations that the reduction of tungsten(V) proceeds directly to tungsten(III).[2]

By further reduction the color turns to wine-red, the oxidation state being slightly higher than +3.[6] So far it has been assumed that the striking color changes accompanying the reduction of chlorotungstates are unequivocally connected with simultaneous changes of the ionic species present. This has led to the belief that the observed color is due to a red tungsten(III) ion, and absorption spectra thereof were reported.[2] Indeed this ion seemed to have been isolated as the pentapotassium tetradecachlorotritungstate(III), $K_5[W_3Cl_{14}]$, as reported by Laudise and Young.[7] The compound has been identified from the product of crystallization of such solutions mainly according to ten additional lines in the X-ray powder photographs. Moreover the well known tripotassium hexachloro-μ-trichloroditungstate(III), $K_3[W_2Cl_9]$, can be precipitated[8,9] after the color becomes the yellow-green characteristic of the $[W_2Cl_9]^{3-}$ ion.

Because of its unusual stereochemistry $K_3[W_2Cl_9]$ has received much attention in the past. An X-ray structure determination,[10,11] magnetic susceptibilities,[12,13] as well as spectroscopic data in the visible[3] and infrared[13] were published. On the other hand, only little is known about the red chlorotungstate(III). Therefore we have reinvestigated the preparation and the properties of $K_5[W_3Cl_{14}]$ as well as the absorption spectrum of the so-called red tungsten(III).

Experimental

Preparation of Complexes.—$K_2[W(OH)Cl_5]$ and $K_3[W_2Cl_9]$ were prepared according to the methods of Olsson[5] and Laudise,[9] respectively. To prevent air oxidation the products were isolated from the corresponding solutions by filtration under a prepurified nitrogen atmosphere and stored in Schlenk-tubes under nitrogen.[14]

The preparation of $K_5[W_3Cl_{14}]$ was attempted several times according to the method of Laudise,[7,15] but without success. In all cases either a mixture of $K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$ or one of these compounds alone was obtained. Variation in temperature, length of reduction, and amount of added KCl resulted only in a change of the ratio of the two compounds.

X-Ray Diffraction.—Powdered specimens of $K_3[W_2Cl_9]$ and of $K_2[W(OH)Cl_5]$ as well as of mixtures of both compounds obtained by the method of Laudise[7,15] were studied by means of X-ray diffraction. Cu Kα radiation was used throughout. A photographic method was applied for the mixtures and both a photographic and a recording method together with a single-circle Philips counter-diffractometer were used for the pure compounds. A comparison of the reflections obtained with those listed by Laudise[16] for his mixture as well as for $K_3[W_2Cl_9]$ is given in Table I. The intensities were estimated visually.

Absorption and Reflection Spectra.—Absorption spectra of chlorotungstates reduced by tin in 12 *M* hydrochloric acid saturated with gaseous HCl were measured with a Beckman DK-2 spectrophotometer. To avoid corrosion the apparatus was purged with prepurified nitrogen. Optical cells with ground-in stoppers were used. For the measurement of $K_2[W(OH)Cl_5]$ solutions in 12 *M* hydrochloric acid under nitrogen optical cells of special design were used.[17] In this case the compound was dissolved in a volumetric flask under nitrogen and the solution filtered into the evacuated cell.

Reflection spectra of $K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$ as well as of mixtures of both prepared according to the method of Laudise[7,15] were measured on the powdered samples using a Zeiss PMQ II spectrophotometer equipped with a reflection attachment RA2. An RCA 1P28 photomultiplier tube served as the detector. Because of the high intensity of some of the absorption bands the samples were diluted with lithium fluoride at ratios of 1:20 or 1:50. The reflection standard used was also lithium fluoride. The powder cups of the apparatus were filled with the powdered samples inside of a glove-box under nitrogen and covered with plates of optical quartz glass to prevent air-oxidation. The partical-size of the samples was less than 5 μ.

Results and Discussion

On the Existence of $K_5[W_3Cl_{14}]$.—The method for the preparation of $K_5[W_3Cl_{14}]$[7,15] produces only mixtures of $K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$; the ratios vary depending on temperature, length of reduction, and the amount of KCl added. The heterogeneity of the product may be detected easily under a microscope: $K_3[W_2Cl_9]$ crystallizes in yellow-green hexagonal plates, whereas $K_2[W(OH)Cl_5]$ forms dark red quadratic-shaped crystals. It is demonstrated also by comparison of the reflection spectra of the products with those of the pure compounds $K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$ (Fig. 1 and 3). In all cases the spectra showed the characteristic bands of these compounds at 19,100 and 22,200 cm.$^{-1}$, respectively, with intensities of these bands roughly corresponding to the ratio of both compounds in the mixture. No additional bands were observed.

According to the X-ray diffraction data reported even the material obtained by Laudise[16] was described as a mixture of $K_5[W_3Cl_{14}]$ with $K_3[W_2Cl_9]$. The diffraction data for $K_3[W_2Cl_9]$ obtained in the present study are in full agreement with those published by Brosset.[10] This is not the case with the data of Laudise,[16] where especially the reflections in the region between $\sin^2 \theta = 0.0973$ and 0.1219 are all missing (see Table I). A detailed comparison of the data compiled in Table I shows that with the exception of a few very weak lines all reflections reported by Laudise for his mixture may be identified either as belonging to the compound $K_3[W_2Cl_9]$ or to $K_2[W(OH)Cl_5]$. This is especially the case with the ten "additional" lines which have been attributed to $K_5[W_3Cl_{14}]$.[18] On the other hand—with the above mentioned restriction—all reflections of either $K_3[W_2Cl_9]$ or $K_2[W(OH)Cl_5]$ may be found in the data reported by Laudise as far as the

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[6] Oxidation numbers between 3.06 and 3.22 have been reported.

[7] R. A. Laudise and R. C. Young, *J. Am. Chem. Soc.*, **77**, 5288 (1955).

[8] H. B. Jonassen, A. R. Tarsey, S. Cantor, and G. F. Helfrich, *Inorg. Syn.*, **5**, 139 (1957).

[9] R. A. Laudise and R. C. Young, *ibid.*, **6**, 149 (1960).

[10] C. Brosset, *Archiv Kemi Mineral. Geol.*, **12A**, 4 (1935).

[11] L. Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

[12] W. Klemm and H. Steinberg, *Z. anorg. allgem. Chem.*, **227**, 193 (1936).

[13] H. B. Jonassen and S. Cantor, *Rec. trav. chim.*, **75**, 609 (1956).

[14] As to the experimental technique see, for example, G. Thomas, *Chem. Ztg.*, **85**, 567 (1961), or S. Herzog and J. Dehnert, *Z. Chem.*, in press.

[15] R. A. Laudise and R. C. Young, *Inorg. Syn.*, **6**, 153 (1960).

[16] R. A. Laudise, Thesis, Massachusetts Institute of Technology, 1956.

[17] H. L. Schläfer and H. Skoludek, *Z. physik. Chem.* (Frankfurt), **11**, 277 (1957).

[18] Mixtures of the two compounds $K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$ obtained by the method cited[15] produced X-ray diffraction patterns of the same kind as those obtained by Laudise.

TABLE I: DATA FROM X-RAY POWDER PHOTOGRAPHS AND FROM DIFFRACTOMETER TRACINGS OF $K_3[W_2Cl_9]$, $K_2[W(OH)Cl_5]$, AND REPORTED DATA OF $K_5[W_3Cl_{14}]$[a]

$K_3[W_2Cl_9]$ + $K_5[W_3Cl_{14}]$ according to Laudise	$K_3[W_2Cl_9]$ Laudise	$K_3[W_2Cl_9]$ Brosset	$K_3[W_2Cl_9]$ this work	$K_2[W(OH)Cl_5]$ this work	Remarks
				0.0077 vw	*b*
0.0089 m	0.0092 s		0.0091 vs		
.0132 s				.0136 vs	
.0154 m	.0154 s		.0155 s		
.0175 m	.0175 s		.0177 vs		
.0234 s				.0234 s	
	.0247 w		.0245 w		
.0257 w					*c*
.0284 w				.0287 m .0305 m	*d*
.0336 w	.0331 m				*e*
.0358 w	.0358 m	0.0357 w	.0362 s		
.0398 w					*f*
.0458 s	.0467 s	.0461 s	.0461 s	.0467 m	
		.0516 vs	.0515 vw		
.0544 s	.0556 s	.0552 m	.0551 m	.0539 vs	*g*
.0597 s				.0593 vs .0602 vs	*h*
	.0618 w	.0615 vw	.0614 vw		
.0635 w	.0643 m	.0638 w	.0637 w		
.0663 w	.0673 m	.0665 w	.0665 w		
.0687 w				.0686 m	
		.0706 vw	.0705 vw		
.0714 s	.0722 s	.0719 vs	.0719 vs		
.0755 s				.0755 w .0769 m	*i*
.0811 s	.0826 s	.0819 s	.0816 s		
.0935 m				.0919 m .0934 vs	*i*
.0973 m	.0976 s	.0968 m .0977 m	.0967 m .0976 m		
				.1060 m	*k*
		.1077 vw	.1077 vw		
		.1099 s	.1098 s		
		.1167 vw	.1170 vw	.1165 vw	
		.1176 m	.1178 m		
.1219 m				.1217 m .1238 w	*i*
.1268 s		.1258 m .1276 s	.1261 s .1273 s		*j*
		.1380 w	.1385 w		
.1429 w	.1429 m	.1425 w	.1428 w		
		.1448 vw	.1446 m		
.1478 w	.1484 w	.1471 vw	.1471 vw	.1471 m	
.1538 w				.1533 w	
		.1602 w	.1596 m		

[a] In the first column are given values of $\sin^2 \theta$ reported for a mixture of $K_3[W_2Cl_9]$ and $K_5[W_3Cl_{14}]$.[16] Values corresponding to lines, which have been assumed as being due to $K_5[W_3Cl_{14}]$, are underlined. Columns 2, 3, and 4 contain values of $\sin^2 \theta$ of $K_3[W_2Cl_9]$ according to measurements of Laudise,[16] Brosset,[10] and the present author, respectively. The values of the last column are mean values of the author's measurements on $K_2[W(OH)Cl_5]$. All values of $\sin^2 \theta$ are given for Cu Kα radiation, where θ is the Bragg angle. The values for $K_3[W_2Cl_9]$ given originally by Brosset for Cr Kα have been converted to those for Cu Kα radiation. The usual intensity notation vs, s, m, w, vw has been used for Brosset's and the author's data, whereas only the classification into s, m, w has been given by Laudise (columns 1 and 2). For convenience lines due to the same compound are tabulated horizontally opposite one another. [b] The first very weak line of $K_2[W(OH)Cl_5]$ appears only on diffractometer tracings and would be placed too close to the primary X-ray beam on a powder photograph. Therefore, it cannot be expected to occur in the data reported by Laudise. [c] The weak line found by Laudise at $\sin^2 \theta = 0.0257$ cannot be identified unambiguously. It is presumably identical with the line found at $\sin^2 \theta = 0.0247$ in the data for $K_3[W_2Cl_9]$. [d] The weak line found by Laudise at $\sin^2 \theta = 0.0284$ can be assigned to the two close lines at $\sin^2 \theta = 0.0287$ and 0.0305 of $K_2[W(OH)Cl_5]$. [e] The weak line reported by Laudise for $K_3[W_2Cl_9]$ at $\sin^2 \theta = 0.0331$ could not be found by the present author and may be due to some unidentified impurity. [f] The weak line observed by Laudise for $K_3[W_2Cl_9]$ + $K_5[W_3Cl_{14}]$ at $\sin^2 \theta = 0.0398$ could not be identified. [g] The strong line reported by Laudise at $\sin^2 \theta = 0.0544$ should correspond both to the line of $K_2[W(OH)Cl_5]$ at 0.0539 and to the line of $K_3[W_2Cl_9]$ at 0.0552, which may not have been separated. [h] The two lines of $K_2[W(OH)Cl_5]$ at $\sin^2 \theta = 0.0593$ and 0.0602 are separated only on diffractometer tracings and, therefore, appear as a unique line at 0.0597 in the photographic data given by Laudise. [i] For these lines a statement similar to that of *h* is valid. [j] For these two lines of $K_3[W_2Cl_9]$ the same holds as stated in *h*. [k] The line of $K_2[W(OH)Cl_5]$ at $\sin^2 \theta = 0.1060$ has not been reported by Laudise for his sample of $K_3[W_2Cl_9]$ + $K_5[W_3Cl_{14}]$. The same is the case for the next four lines of $K_3[W_2Cl_9]$. Therefore, in the data reported by Laudise for $K_3[W_2Cl_9]$ and for the $K_3[W_2Cl_9]$–$K_5[W_3Cl_{14}]$ mixture, all lines expected in the region between $\sin^2 \theta = 0.0973$ and 0.1219 are missing.

region of his measurements is covered.[19] Therefore it is obvious that $K_5[W_3Cl_{14}]$ is the compound $K_2[W(OH)Cl_5]$ described by Olsson.[5]

The analytical data obtained by Laudise[16] are rather inconclusive, because even though they are close to the empirical composition of $K_5[W_3Cl_{14}]$ they lie between those calculated for $K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$, respectively (Table II).

TABLE II

ANALYTICAL DATA

	Theoretical			
	$K_3[W_2Cl_9]$	$K_2[W(OH)Cl_5]$	$K_5[W_3Cl_{14}]$	Found[16]
W	45.7	40.3	44.4	43.8
Cl	39.7	38.8	39.9	39.3
K	14.6	17.1	15.4	15.9

The observations reported[16] as being due to the equilibrium $3[W_2Cl_9]^{3-} + Cl^- \rightleftharpoons 2[W_3Cl_{14}]^{5-}$ are only of a qualitative nature and are therefore open to criticism. Indeed the existence of this equilibrium could not be verified in the present study.[20]

Reflection Spectrum and Disproportionation of $K_2[W(OH)Cl_5]$ in Solution.—The compound $K_2[W(OH)Cl_5]$ has some unusual spectral properties. The reflection spectrum measured on powdered samples under an inert gas atmosphere is displayed in Fig. 1 and the spectral data are summarized in Table III.

TABLE III

SPECTRAL DATA OF $K_2[W(OH)Cl_5]$

Wave length λ, mμ	Wave number $\bar{\nu}$, cm.$^{-1}$	Extinction coeff. ϵ^a
(780)^b	12,800	<100
524^c	19,100^c	~10,000
(436)	22,900	<400
390	25,600	
300	33,300	
254	39,400	
228	43,900	

^{a} Estimated from the absorption spectrum. ^{b} Numbers in parentheses indicate shoulders. ^{c} Values obtained from the absorption spectrum; in the reflection spectrum the band maximum has been found at 535 mμ (18,700 cm.$^{-1}$).

Besides some weak bands in the region between 31,000 and 22,000 cm.$^{-1}$ and two charge-transfer bands of the ligands in the ultraviolet it shows an absorption band of high intensity at 19,100 cm.$^{-1}$ (524 mμ), which accounts for the deep violet color of its solutions. The extinction coefficient of this band of course cannot be estimated from the reflection spectrum.

In aqueous as well as in hydrochloric acid solution the compound is fairly unstable, and the deep violet color observed immediately after dissolution soon changes into wine-red and finally into yellow-green. The rate of decomposition is dependent to a high degree on the concentration of Cl^- ions in solution and may be decreased considerably by adding LiCl.[21] In this case the decomposition can be followed spectrophotometrically and absorption spectrum *vs.* time plots as shown in Fig. 2 are obtained.

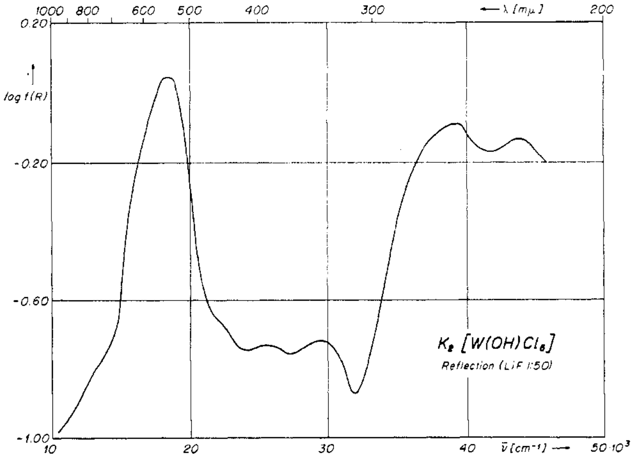

Fig. 1.—Reflection spectrum of $K_2[W(OH)Cl_5]$. On the ordinate the logarithm of the Kubelka–Munk function log f(R) is plotted, where f(R) = $(1 - R)^2/2R$, R being the relative reflectance of the sample. The sample has been diluted with LiF to the ratio of 1:50.

In a solution containing 5 g. of LiCl per 100 ml. the extinction coefficient of the band situated at 19,100 cm.$^{-1}$ is still ~3000 even 14 min. after dissolution (Fig. 2). During the first 14 min. the absorption is too intense to be measured by the spectrophotometer working at a concentration of 10^{-3} M and with a path length of 1 cm. A linear extrapolation of the values of log ϵ_{max} plotted *vs.* time to $t = 0$ indicates that the extinction coefficient of the band at 19,100 cm.$^{-1}$ should be ~10,000. Because of the exponential form of the rate law the extinction coefficient might really be still higher.[22]

Such bands of high intensity in the visible region of the absorption spectra of coordination compounds are usually associated with species containing an element in two different oxidation states.[23] A suspicion that the compound $K_2[W(OH)Cl_5]$—apparently tungsten(IV)—might instead be a compound of tungsten(V) and tungsten(III) has also been raised by Collenberg[4a] on account of his observation that $K_3[W_2Cl_9]$ is formed during the electrolytic reduction of tungsten(VI) long before the over-all oxidation state of +4 has been reached. Besides it is supported by the findings of Lingane[2] that the reduction in solution takes place directly from the oxidation state +5 to +3. Nevertheless, the real chemical constitution of this compound is still unexplained[24] and would most likely be clarified by an X-ray structure determination.

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[19] The reflections at $\sin^2 \theta > 0.1538$ were disregarded, because no data were given by Laudise in this region. Since in the present work the main purpose has been to obtain data which might easily be compared with those of Laudise, it was also resigned from investigations of the X-ray diffraction of single crystals.

[20] However, notice below the dependence of the decomposition of $K_2[W(OH)Cl_5]$ on the Cl^- ion concentration.

[21] For example, the seventh absorption curve in Fig. 2 has been observed after 13 min. in 12 M HCl, but only after 40 min. in 12 M HCl to which 5 g. of LiCl per 100 ml. have been added.

[22] Compare also with the former measurements of Jørgensen[3] giving ϵ ~600 which might have been affected by partial decomposition.

[23] Compare, for example, with the absorption spectrum of Prussian blue, M. B. Robin, *Inorg. Chem.*, **1**, 337 (1962).

[24] The chemical and physical properties of this compound are under active investigation at this laboratory.

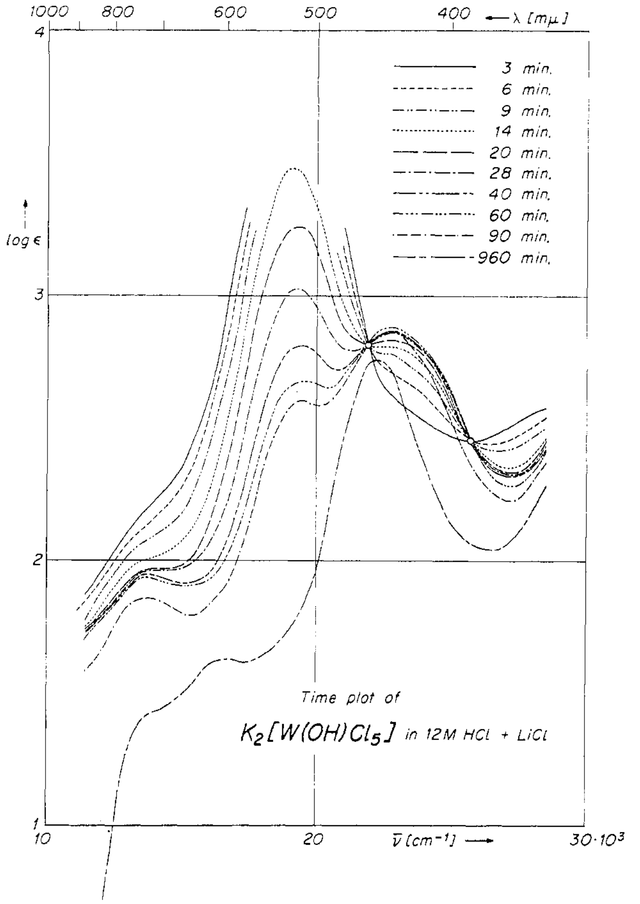

Fig. 2.—Time plot of the absorption spectrum of $K_2[W(OH)Cl_5]$ in 12 *M* hydrochloric acid (initial concentration 10^{-3} *M*, path length 1 cm.).

The evident instability of solutions of $K_2[W(OH)Cl_5]$ is unaffected by providing an atmosphere of prepurified nitrogen. Thus the observed decomposition cannot be effected by an air oxidation as assumed previously.[5]

An explanation is offered by considering the changes in the absorption spectra. The fact that during the first 60 min. of the decomposition reaction all absorption spectra intersect in two isosbestic points (Fig. 2) deserves particular attention, because it provides evidence that during this time only one reaction occurs.[25]

The changes in the absorption spectrum consist of a successive lowering of the 19,100 cm.$^{-1}$ band and a simultaneous raising of a new band at $\sim$22,730 cm.$^{-1}$, the extinction coefficient becoming $\sim$760 after 60 min. In addition, a second band of low intensity appears at $\sim$13,500 cm.$^{-1}$. After more than 60 min., the lowering of the 19,100 cm.$^{-1}$ band proceeds further, and the 22,730 cm.$^{-1}$ band shifts slowly to lower wave numbers, losing some intensity. At the same time the two isosbestic points start to disappear, indicating that a second reaction is taking place. Finally after 16 hr. the 22,730 cm.$^{-1}$ band has been displaced to 22,200 cm.$^{-1}$ and two additional bands of low intensity can be recognized at $\sim$13,500 and $\sim$16,500 cm.$^{-1}$.

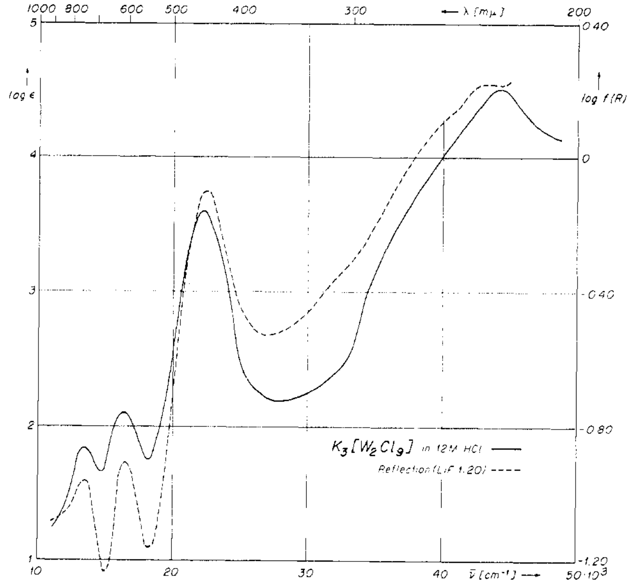

Fig. 3.—Absorption and reflection spectrum of $K_3[W_2Cl_9]$. On the left ordinate log ϵ of the absorption spectrum is plotted, and on the right the logarithm of the Kubelka-Munk function log f(*R*) is plotted, where $f(R) = (1 - R)^2/2R$, *R* being the relative reflectance of the sample. The sample has been diluted with LiF to the ratio of 1:20.

Comparison with the absorption spectrum of the pure compound $K_3[W_2Cl_9]$ (Fig. 3) shows clearly that the ion $[W_2Cl_9]^{3-}$ is one product of the decomposition. Therefore it is to be expected that the first reaction should be a disproportionation of $K_2[W(OH)Cl_5]$ into tungsten(V) and tungsten(III) compounds. There are two possible explanations of the changes in absorption spectra observed:

(1) The tungsten(III) product of the first reaction is the ion $[W_2Cl_9]^{3-}$; the observed peak displacement from 22,200 to $\sim$22,730 cm.$^{-1}$ could be caused by the contribution of a weak band of $K_2[W(OH)Cl_5]$ at $\sim$22,900 cm.$^{-1}$ (Fig. 1). The second reaction is presumably an oxidative decomposition of $K_3[W_2Cl_9]$ and/or a conversion into other forms of tungsten(III).[26]

(2) The tungsten(III) product of the first reaction might be another form of tungsten(III) with an absorption peak at $\sim$22,730 cm.$^{-1}$ and ϵ $\sim$1500. The second reaction would then be a (partial) conversion into the $[W_2Cl_9]^{3-}$ ion, which finally undergoes an oxidative decomposition.[26]

No evidence could be obtained as to the ionic species of tungsten(V) produced simultaneously during the disproportionation because of the low intensity of its spectrum.[3] The transient red color of the solution observed during the first minutes of the first reaction[27] cannot be assigned to an individual red tungsten(III) but is caused rather by superposition of the absorption spectra of $K_2[W(OH)Cl_5]$ and $K_3[W_2Cl_9]$.

Red Tungsten(III).—Even though the material described by Laudise,[7] which consists of a mixture of

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[25] H. L. Schläfer and O. Kling, *Angew. Chem.*, **68**, 667 (1956); O. Kling and H. L. Schläfer, *Z. Elektrochem.*, **65**, 142 (1961).

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[27] The explanation (2) cannot be used in favor of the existence of a red tungsten(III), because at the end of the first 60 min., when the peak at $\sim$22,730 cm.$^{-1}$ obtains its maximal value, no tinge of red is left and the solution becomes a yellow-green.

$K_3[W_2Cl_9]$ and $K_2[W(OH)Cl_5]$, dissolves to form a red solution, the impressive wine-red color observed during the *reduction* of chlorotungstates[28] is still unexplained. Therefore we have measured the absorption spectra of samples taken after different reduction times from chlorotungstate solutions reduced with tin below the oxidation state +4. All the spectra of red solutions obtained in this way showed two bands at 19,100 and ~22,730 cm.$^{-1}$, respectively, with different intensity ratios depending on external conditions. They usually fit into the sequence of spectra obtained in Fig. 2.

Therefore, even if the results available at present are not sufficient to disprove the existence of a red tungsten(III) definitely, it seems probable that the existence of red tungsten(III) is simulated during the reduction of chlorotungstates in a like manner as in the case of the disproportionation of $K_2[W(OH)Cl_5]$. The red solutions simply contain the two ions $[W_2Cl_9]^{3-}$ and $[W(OH)Cl_5]^{2-}$. If this is assumed to be the case, all the former observations of red tungsten solutions[28] obtained as the product of reduction of tungsten(VI) may easily be understood because of the very high intensity of the 19,100 cm.$^{-1}$ band in the absorption spectrum of $K_2[W(OH)Cl_5]$.[29]

Apparently the formation of $K_2[W(OH)Cl_5]$ from tungsten(V) and from tungsten(III) complex ions during the reduction of chlorotungstates in strong HCl, as well as its disproportionation into these ions, follow reaction schemes that may be closely related. Which one of these reactions is preferred seems to depend on the concentration of the tungsten species involved as well as on the concentration of Cl^- ions only.

Acknowledgments.—This investigation has been partly carried out at the Institute of Physical Chemistry, University of Frankfurt (Main), Germany. The author is grateful to Professor H. Hartmann and Professor H. L. Schläfer for providing the facilities. Thanks are due to Dr. H. J. Bielen and F. Weber, Institute of Mineralogy, for valuable help in taking X-ray powder patterns, and to Dr. R. A. Laudise, Bell Telephone Laboratories, Murray Hill, N. J., for communication of his results. The assistance of Dr. R. Feltham in preparing the manuscript is also gratefully acknowledged.

[28] (a) Olsson[5] observed that during the reduction of chlorotungstates in strong HCl with tin a transient red solution is formed. (b) Using a lead cathode Collenberg and Backer[4a] obtained red solutions with a tinge of yellow and an oxidation number of +3.02 by reduction of potassium chlorotungstate solutions in concentrated HCl at 18°. Higher temperatures (35 to 50°) produced directly the yellow-green $[W_2Cl_9]^{3-}$ ion. Sometimes the reduction of sodium chlorotungstate solutions produced clear red solutions with oxidation numbers >3.06. From these solutions RbCl precipitated a dark red substance, an empirical formula $Rb_2[W(H_2O)Cl_5]$ having been proposed, but the authors confess that the composition of different preparations fluctuated widely. (c) Lingane and Small[2] obtained red tungsten solutions during the coulometric reduction of tungsten(V) in 12 *M* HCl at 18°, the oxidation state having been found to be +3.09. The existence of a red tunsten(III) has been postulated and an absorption spectrum exhibiting one single band at 19,050 cm.$^{-1}$ (ϵ ~560) was reported. They avoided carrying out the reduction to completion, because then the yellow-green $[W_2Cl_9]^{3-}$ ion is obtained. (d) Laudise and Young[7] reported the preparation of $K_5[W_3Cl_{14}]$, the $[W_3Cl_{14}]^{5-}$ ion having been reported as giving a deep red solution with an absorption band at 19,400 cm.$^{-1}$. They found an oxidation state of +3.22; as to the nature of this substance see above. (e) Hawkins and Garner[26] observed that during the decomposition of the $[W_2Cl_9]^{3-}$ ion the solutions often turn red and at the same time a broadening of the base of the 22,200 cm.$^{-1}$ peak has been observed.

[29] In consequence of the high intensity of the 19,100 cm.$^{-1}$ peak (ϵ ~10,000) of $K_2[W(OH)Cl_5]$, solutions containing almost the total tungsten as tungsten(III) and only a small part as $K_2[W(OH)Cl_5]$ may still be red or even show a tinge of red. Therefore usually an oxidation state slightly higher than +3.00 has been found for the so-called "red tungsten(III)" solutions.[28b,c,d]

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Thermodynamics of Metal–Halide Coordination in Aqueous Solution. I. Equilibrium Constants for Several Mercury(I)- and Mercury(II)-Halide Systems as a Function of Temperature[1a]

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Received May 25, 1963

Equilibrium constants have been determined for the stepwise formation at 7 and 40° of $HgX_2(aq)$ (X = Cl, Br, I) from Hg^{+2} and X^- (also at 25° in the case of Cl^-). Solubility product constants for Hg_2X_2 at 7 and 40° and the solubility of HgI_2 at 8, 25, and 40° have also been determined. All data are valid in a solvent 0.10 *F* in $HClO_4$ and 0.40 *F* in $NaClO_4$.

Introduction

Important theoretical advances[2,3] in recent years have resulted in a better understanding of the nature of the bonding forces in coordination compounds. However, the quantitative thermodynamic data needed to evaluate these theories in the case of complex ions in aqueous solution are, in many cases, not known. Particularly scarce are calorimetrically determined $\Delta H°$ and corresponding $\Delta S°$ values for metal–ligand interaction.

Extensive studies[4,5] of the stabilities of halide complexes of the elements in aqueous solution indicate that

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[1] (a) Supported by the Atomic Energy Commission, Contract No. AT(04-3)-299. Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963. (b) To whom correspondence concerning this article should be addressed.

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