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Complexes of Tungsten(III)

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When $K_3W_2Cl_9$ is refluxed under anhydrous anaerobic conditions in pyridine or aniline three chloride ions are displaced and the non-electrolytes $W_2Cl_9(C_5H_5N)_3$ or $W_2Cl_9(C_5H_5NH_2)_3$ are formed. Analyses, equivalent weight determinations and infrared data indicate that the space configuration of these new complexes are the same as the original $(W_2Cl_9)^{3-}$ ion. Slow rate and rigorous conditions for displacement indicate non-labile inner orbital complex exchange.

Introduction

Previous investigations on trivalent tungsten have produced two types of compounds of the enneachloroditungstate ion, $(W_2Cl_9)^{3-}$. The two varieties are those containing alkali, ammonium or thallos cations, as in $K_3W_2Cl_9$, while the second type consists of cationic ammine complexes illustrated by $[Co(NH_3)_6]W_2Cl_9$ and $[Ag(NH_3)_2]_3W_2Cl_9$.

Brosset,¹ who studied some of these salts by powder X-ray diffraction methods, proved that the ion consists of two fused octahedra with a common triangular face of chloride ions. Each tungsten atom has six equidistant chloride ions at a distance of 2.45 Å. A remarkable structural feature of the enneachloroditungstate ion is the short tungsten-tungsten bond distance of 2.46 Å. This value is even less than the metallic tungsten-tungsten bond which is 2.74 Å, which suggests that the tungsten-tungsten bond in the $(W_2Cl_9)^{3-}$ ion is multiple. Brosset's results were verified by Pauling.²

The diamagnetic character of the ion can be partially explained by assuming a d^2sp^3 hybridization for each tungsten ion which also contains three single electrons in three 5d orbitals of each tungsten. In order to fully explain the diamagnetism, it is necessary to postulate a coupling of the 5d orbitals between the tungsten ions, *i.e.*, a triple bond.

Sidgwick³ has indicated that since salts of the $(W_2Cl_9)^{3-}$ ion were the only known compounds of tungsten(III), these compounds may be thought of as derivatives of a dimeric chloride unit, W_2Cl_6 . It would be expected that these ions could be oxidized by even weak oxidizing agents and such is the case with $K_3W_2Cl_9$ first prepared by Olsson.⁴

The purpose of the present investigation was to stabilize the trivalent state by complex ion formation with pyridine and aniline, to see what compounds are formed with these complexing agents, and to elucidate some features of the stereochemical structure of these new compounds.

Experimental

1. Preparation of Compounds. A. Potassium Enneachloroditungstate.—When a tungstate ion is reduced electrolytically in concentrated hydrochloric acid the enneachloroditungstate ion is obtained. The method of preparation is quite detailed and may be found elsewhere.⁵ Starting with 50 g. of $WO_3 \cdot H_2O$, 27 g. of $K_3W_2Cl_9$ was obtained, corresponding to a yield of 34%.

(1) C. Brosset, *Nature*, **135**, 874 (1935).

(2) L. Pauling, *Chem. Eng. News*, **25**, 2970 (1937).

(3) N. V. Sidgwick, "Chemical Elements and Their Compounds," University Press, Oxford, 1950, p. 1059.

(4) O. Olsson, *Ber.*, **46**, 566 (1913).

(5) H. B. Jonassen, S. Cantor and A. Tarsey, "Inorganic Syntheses," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1955, Chapter XXX.

B. Pyridine Complex.—Ten grams of freshly recrystallized potassium enneachloroditungstate was refluxed with 150 ml. of fractionally distilled pyridine under dry, deoxygenated nitrogen for six hours. The liquid phase turned a dark shade of red after just a few minutes, while the solid phase turned brown. After six hours the red solution was filtered from the brown colored precipitate. This brown material was washed with ether and boiling water until no potassium ions remained. Tungsten and chlorine analyses indicated a non-stoichiometric material. A dark brown precipitate was formed from the filtrate upon the addition of large amounts of ether (at least 10 ml. of ether for every ml. filtrate). This precipitate was recrystallized from pyridine. The substance was analyzed for tungsten, chlorine and nitrogen by the methods indicated below. In addition, the oxidation state, magnetic susceptibility and absorption characteristics were determined. *Anal.* Calcd. for $W_2Cl_9(C_5H_5N)_3$: W, 45.0; Cl, 26.0; N, 5.13; equiv. wt., 136. Found: W, 44.8; Cl, 26.3; N, 5.17; equiv. wt., 139.

The compound was found to be diamagnetic. The infrared absorption spectra are shown in Fig. 1.

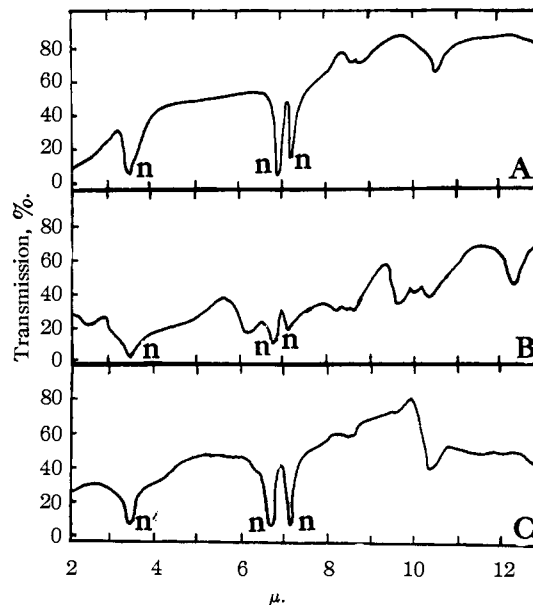


Fig. 1.—Infrared absorption spectra: A, $K_3W_2Cl_9$; B, $W_2Cl_9(C_5H_5N)_3$; C, $W_2Cl_9(C_5H_5NH_2)_3$. All spectra of about 0.2 g. of solid, powdered, milled with a drop of Nujol, and pressed between two rock salt plates, *i.e.*, practically zero depth. A Perkin-Elmer Model 21 instrument was used. Transmission minima due to Nujol are referred to by "n."

C. Aniline Complex.—The method and quantities were precisely those of the pyridine reaction except, of course, that the refluxing temperature was higher. The liquid phase slowly turned dark brown. There was very little precipitate formed even after several runs. The reaction was allowed to run for 12 hours. The filtrate was mixed with excess ether which resulted in a dark brown precipitate which was recrystallized from aniline.

Anal. Calcd. for $W_2Cl_9(C_5H_5NH_2)_3$: W, 42.8; Cl, 24.7; N, 4.89. Found: W, 43.5; Cl, 23.9; N, 4.86.

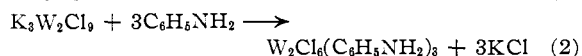
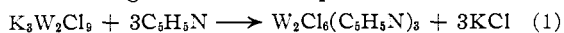
The compound was found to be diamagnetic. No absorption maxima were found in the visible region. The infrared absorption spectrum is shown in Fig. 1.

2. **Methods.**—Tungsten analyses were determined by allowing the sample to react with hot 6 *N* nitric acid, digesting, filtering and igniting. Nitrogen analyses were carried out by both Dumas and Kjeldahl techniques. Chlorine analyses were made by a distillation method in which the sample is treated with 36 *N* sulfuric acid and then heated, with the product hydrogen chloride gas swept with nitrogen into a 10% solution of sodium hydroxide. The reaction mixture was heated and swept for three hours. To make sure all chlorine had been volatilized, a saturated aqueous solution of $K_2Cr_2O_7$ was added to the reaction, heating and sweeping further for two hours. The absorbed basic chloride was neutralized with *N* nitric acid and determined gravimetrically by silver ion addition.

Equivalent weights were determined by boiling a sample with an excess of standard potassium dichromate. The remaining dichromate was then destroyed by allowing it to oxidize iodide to iodine which was then titrated with thiosulfate using starch indicator. It was found that a sample of pyridine complex weighing 0.0139 g. used 0.1004 equivalent of thiosulfate less than a blank under identical conditions. The magnetic susceptibilities were determined on a Curie-Cheveneau type balance. Visible spectra were determined on a Beckman Model B Spectrophotometer. Infrared spectra were run on a Perkin-Elmer Model 21 using Nujol mull and KBr pressed disc techniques with the former giving better results.

Results and Discussion

The visible absorption spectrum of the pyridine complex showed that there were two absorption maxima, one at 345 $m\mu$ and the other at 510 $m\mu$. Figure 1 shows a comparison of infrared absorption spectra of the three complexes indicated. It will be noticed that there is a retention of the broad bands at 8.7 and 10.4 μ . For potassium enneachloroditungstate, the only peaks in the rock salt regions are those mentioned and these are retained with only slight deviation by the pyridine and aniline derivatives. The retention of bands suggests that the same bands present in the parent substances are present in the derivatives. The analyses show that the following reactions took place

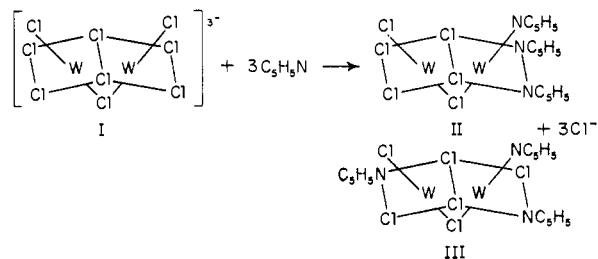


Qualitative reagent and flame photometry checks did not reveal the presence of any potassium ions in the complexes.

Unlike the starting enneachloroditungstate, the tris-pyridine and tris-aniline complexes are insol-

uble in water, but are partially soluble in non-polar solvents such as ether and benzene. This is no doubt due to the covalent nature of the complex formed.

If the double fused octahedron is represented as I, the course of the reaction may be illustrated structurally as



It would be extremely difficult to determine by a simple chemical or physical means whether II or III or a combination of both is formed. It is quite improbable that the chlorides of the shared triangular face are displaced since pyridine is not known to act as a bridging group. What occurs in the pyridine complex formation, applies also to the aniline complex.

The rather rigorous conditions employed in carrying out these displacement reactions is well explained by Taube's hypothesis of labile and non-labile inner orbital complexes.⁶ Each WCl₆ octahedron in the enneachloroditungstate ion has a tungsten(III) ion with at least one electron in all 5d orbitals. The difficulty in forming a heptacoordinate intermediate is reflected in the reflux conditions for the chloride displacement by the complexing agents.

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NEW ORLEANS, LA.

(6) H. Taube, *Chem. Revs.*, **50**, 69 (1952).