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New syntheses of tungsten(IV) halides and their adducts with nitrogen and sulfur donor ligands. Characterization by vibrational spectroscopy and study of magnetic properties

by

Margaret Anne Schaefer

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INTRODUCTION

Very few studies have been made of the magnetic properties of complexes containing two d electrons. Those made have predominately involved first row transition elements. For this reason it was felt that a study of a series of tungsten (IV) complexes would be of value.

The purpose of this study was to devise reliable methods for synthesizing tungsten(IV) complexes, to characterize these complexes by use of infrared spectroscopy and to investigate their magnetic properties. Since tungsten(IV) halide complexes have been found to be relatively stable it was decided to prepare a series of tungsten(IV) chloride adducts WCl_4L_2 with L a variety of ligands, in particular nitrogen and sulfur donors.

These tungsten(IV) complexes provide examples of d^2 systems where there is a large spin-orbit coupling effect. Since the symmetry of the environment around the metal is lower than cubic (D4h if the ligands are trans, C2v if they are cis) they also provide a means of observing the effects of low symmetry on the magnetic properties of the system.

Review of Previous Work

Preparation of tungsten(IV) and molybdenum(IV) halide complexes have, in general, utilized three basic methods: (1) reduction of a higher valent halide using the ligand as a reducing agent, (2) oxidation of a lower valent complex using a halogen as the oxidizing agent, and (3) direct reaction of a tungsten(IV) halide or halide complex with the desired ligand. Four types of complex have been reported: those with nitrogen donor ligands; those with phosphorus or arsenic donor ligands; those with sulfur or oxygen donor ligands; and anionic complexes.

Anionic complexes

Edwards, Peacock and Said (1) prepared the complex chlorides and bromides of molybdenum(IV) under anhydrous conditions and studied their chemical and magnetic properties. The hexachloromolybdate(IV) anion was synthesized by interaction of molybdenum pentachloride with an alkali metal chloride at 150° using iodine monochloride as the solvent. Pure complexes, $M^{I}_{2}MoCl_{6}$, were isolated (M^{I} = K, Rb, Cs). To obtain Tl_2MoCl_6 it was necessary to use TlI rather than TlCl. Two hexabromomolybdate(IV) complexes, Rb_2MoBr_6 and Cs_2MoBr_6 were prepared by heating $MoBr_3$, alkali metal bromide, and IBr at 300°. Both the bromide and chloride complexes had the cubic K_2PtCl_6 structure. The magnetic moment of the chloride salts ranged from 2.24 to 2.28 B.M. and that of the bromide salts from 2.08 to 2.18 B.M. The complexes exhibited Curie-Weiss behavior from 80° to 300°K. The Curie constants θ ranged from 54° to 160°K for the chlorides, and 160° to 200°K for the bromides.

Fowles and coworkers (2) prepared $M^I{}_2MoCl_6$ (M^I = Rb, Cs, C_5H_5NH, C_9H_8N, $(C_2H_5)_2NH_2$) by interaction of alkali metal halide with $MoCl_5$ or the amine hydrochloride with $MoCl_4(CH_3CH_2CH_2CN)_2$ in chloroform. Magnetic moments were found to range from 2.13 to 2.30 B.M.

One of the earliest reports of a tungsten(IV) complex was the preparation of K_2WCl_5OH by Klemm and Steinberg (3). Tungsten trioxide was reduced in concentrated hydrochloric acid in the presence of potassium chloride to yield the red crystalline compound. The room temperature magnetic moment was found to be 2.20 B.M. However, polarographic studies by Lingane (4) of tungsten in hydrochloric acid solution indicated that under the conditions investigated tungsten goes immediately from the +5 to the +3 oxidation state. He suggested that K_2WCl_5OH was a binuclear complex with one tungsten in the +5 and the other in the +3 oxidation state. König studied the absorption spectra and found an intense absorption at 19,900 cm^{-1} ($\varepsilon_{mol} > 10^4$) (5). He felt this might indicate a binuclear mixed oxidation state complex. He also found that the compound decomposed in solution in the absence of excess chloride ion. One of the major decomposition products was $[W_2Cl_9]^{3-}$. Siefert and Wöhrmann (6) prepared $[N(CH_3)_4]_2WCl_6$ by electrolytic reduction of WCl_6 in methanol saturated with HCl. Tetramethylammonium chloride was added to precipitate the salt. The structure was isomorphous with K_2PtCl_6 and the magnetic moment was 1.68 B.M., a value which was unchanged down to 82°K. Electrolysis of WCl_6 in methanol with no HCl added gave $[N(CH_3)_4]_2WCl_5(OCH_3)$. The magnetic moment was 1.55 B.M., and as with the hexachlorotungstate(IV) complex, the magnetic moment was constant down to 92°K.

Brisdon, Fowles and Osborne (7) reported that aliphatic amines react with WCl_6 under anhydrous conditions to give amine salts containing the hexachlorotungstate(IV) anion. Both secondary and tertiary amines were used. The main products were $(NH_2R_2)_2WCl_6$ and $(NHR_3)WCl_6$ ($R = CH_3$, C_2H_5). Other products of the reactions were not identified. The authors suggested a free radical mechanism for the reduction reaction.

By using reaction conditions similar to those used to prepare the hexahalomolybdate(IV) salts, Kennedy and Peacock (8) synthesized salts containing the hexachlorotungstate(IV) and hexabromotungstate(IV) anions. Reaction of WCl_6 or WBr_6 and the iodide of the cation at 130° yielded $M^I_2WCl_6$ and $M^I_2WBr_6$. The chloride salts of K, Rb, Cs, Tl and Ba were prepared and the Cs, Rb, and K salts of the bromide. With the exception of $BaWCl_6$ and K_2WBr_6 all were isomorphous with K_2PtCl_6. Magnetic moments were lower than those of the corresponding molybdenum salts, 0.89 to 1.47 B.M. for the chlorides, and 1.50 to 1.72 B.M. for the bromides. Plots of $1/\chi'_M$ vs. T were linear; Curie temperatures θ were 180° to 400°K for the chloro complexes and

137° to 200°K for the bromo complexes. Because of the high Curie temperatures the authors suggested the possibility of antiferromagnetic interactions through neighboring chloride ions.

Complexes with nitrogen donors

The greatest number of complexes of tungsten(IV) and molybdenum(IV) have been with ligands which are nitrogen donors. A series of nitrile adducts were synthesized by Fowles and coworkers (9). They prepared the chlorides and bromides of tungsten and the chlorides of molybdenum. When they stirred any of the higher valent halides in excess nitrile, RCN (R = CH_3, C_2H_5, C_3H_7) the tetravalent complexes were produced. The magnetic moments of the chloride complexes were about 2.5 B.M. for the molybdenum, and 1.78 to 2.07 B.M. for the tungsten derivatives. The moments of the bromides were 0.1 to 0.2 B.M. lower than for the chlorides. The magnetic moment of $MoCl_4(CH_3CH_2CN)_2$, $WCl_4(CH_3CH_2CN)_2$, and $WBr_4(CH_3CN)_2$ were observed at four temperatures from 90° to 295°K. The Curie-Weiss law was obeyed with a Curie temperature of 40°K for the molybdenum complexes and 250°K for the tungsten complexes.

A number of workers have studied MX_4 adducts with pyridine and substituted pyridines. Kennedy and Peacock (8) dissolved K_2WCl_6 and K_2WBr_6 in pyridine. The products recovered from solution were $WCl_4(C_5H_5N)_2$ and $WBr_4(C_5H_5N)_2$.

Difficulties were encountered in separating the potassium halide formed in the reaction from the desired product. They found a magnetic moment of 2.06 B.M. for $WCl_4(py)_2$ (py = C_5H_5N). A study of the temperature dependence of the susceptibility was made from 90° to 290°K. The authors suggested that this complex was antiferromagnetic with a Neél minimum occurring at 100°K, though this observation was based on the behavior of a small number of data points near 90°K. The room temperature magnetic moment of $WBr_4(py)_2$ was found to be 2.03 B.M. The complex exhibited Curie-Weiss behavior with a θ value of 1.80°K.

McCarley and Brown (10) prepared the pyridine adducts of tungsten(IV) chloride and bromide by interaction of the tetrahalides with neat pyridine. They also found that reaction of WCl_6, WCl_5, or WBr_5 with pyridine proceeded with reduction of the metal to yield the tungsten(IV) halide dipyridine adducts. Brown (11) studied the magnetic properties of $WX_4(py)_2$ (X = Cl, Br) prepared by reaction of the tetrahalides with pyridine. He found the magnetic moments to be 1.6 and 2.1 B.M. for the chloride and bromide respectively. A study of the temperature dependence of the magnetic susceptibility revealed no evidence of the Neél point reported by Kennedy and Peacock. The values of the susceptibility that Brown observed were in general lower than those Peacock reported and plots of χ_m vs 1/T showed greater curvature over the same temperature range.

Blight and Kepert (12) prepared $WCl_4(py)_2$ by stirring $WCl_4(CH_3CN)_2$ in a mixture of pyridine and acetonitrile. They claimed that reaction of WCl_4 with pyridine at room temperature gave a mixture of tungsten(IV) and tungsten(III) complexes, whereas refluxing WCl_4 in pyridine effected complete reduction to $WCl_3(py)_2$. These observations were based on X-ray powder pattern data for the products obtained under these conditions. They found a room temperature magnetic moment of 1.29 B.M. for $WCl_4(py)_2$ and a θ value of -2°K from a Curie-Weiss treatment of the data from 90° to 300°K. Their values of magnetic susceptibility were lower than those reported by both Kennedy and Peacock, and Brown.

Converse (13) also measured the magnetic susceptibility of samples of $WCl_4(py)_2$ and $WBr_4(py)_2$ prepared by reduction of the pentahalides in pyridine. His data were in agreement with those of Brown. The magnetic moment at 300°K of the chloride was 1.77 and the bromide 1.67 B.M. He also found no evidence of a Neél point down to 77°K.

Larson and Moore (14) prepared the analogous molybdenum (IV) complex $MoCl_4(py)_2$ by reaction of $MoCl_4$ with neat pyridine. They observed a magnetic moment of 2.52 B.M. at room temperature. Allen, Feenan and Fowles (15) studied the same compound along with complexes of various other pyridine derivitives. They prepared bis adducts, $MoCl_4L_2$ with L = pyridine, α-picoline, pyrazine, and 2,6-dimethylpyrazine. The bipyridine monoadduct was also obtained. The compounds were synthesized by displacement of the nitrile in $MoCl_4(CH_3CH_2CH_2CN)_2$. They found μ = 2.71 B.M. for the pyridine, and 2.36 B.M. for the bipyridine adduct. A very small θ value was observed when their data were fitted to the Curie-Weiss equation over a range of temperatures from 80° to 300°K.

Walton and coworkers (16) prepared $MoCl_4$(bipy) (bipy = 2,2'-bipyridine) by reaction of $MoCl_5$ with bipyridine in dry ether, and also by direct reaction of $MoCl_4$ with bipyridine in dichloromethane. Solutions of $MoCl_4$(bipy) in nitromethane or acetonitrile were found to be weakly conducting but values of the conductance were well below that predicted for a 1:1 electrolyte in these solvents. The magnetic moment of the complex obtained by reduction of $MoCl_5$ with bipyridine was measured from 81° to 302°K. The magnetic moment was virtually temperature independent over this range (2.35-2.37 B.M.) and the θ value obtained from a Curie-Weiss plot was only 3°K.

The oxidation of $Mo(CO)_4$(bipy) by halogens was utilized by Hull and Stiddard (17) to obtain both MoX_4(bipy) and WX_4(bipy) (X = Cl, Br). From study of the far infrared spectra in the metal-halogen stretching region (200-400 cm^{-1}) the cis configuration was assigned to all four complexes. Two or three bands were found in this region for all the compounds. The room temperature magnetic moments were the following: $MoCl_4$(bipy), 2.36 B.M.; $MoBr_4$(bipy), 2.36 B.M.;

WCl_4(bipy), 1.64 B.M.; WBr_4(bipy), 1.69 B.M.

Complexes with arsenic and phosphorus donors

Nigam, Nyholm, and Stiddard (18) did a similar oxidation of $Mo(CO)_4$(diars) (diars = o-phenylene bis dimethylarsine) with bromine to give $MoBr_4$(diars). As with $MoCl_4$(bipy), the complex had a slight conductivity in benzene, about one-fifth that predicted for a 1:1 electrolyte. The magnetic moment at 293°K was 1.96 B.M.

A preparation of WCl_4(biphos), (biphos = bis 1,2-diphenylphosphinoethane) was reported by Boorman, Greenwood, and Hildon (19). They fused K_2WCl_6 with biphos at 220° for 2 hours. This gave a yellow brown powder which analyzed as WCl_4(biphos). A cis configuration was assigned because of the bidentate character of the ligand and because four bands were observed in the metal-chloride stretching region. The magnetic moment was 1.74 B.M. at 273°K. They reported an isomeric complex formed by reaction of K_2WCl_6 or $WCl_4(CH_3CN)_2$ with biphos in either acetonitrile or benzene. This compound analyzed as WCl_4(biphos) but was an electrolyte in nitromethane and has a molecular weight of 660 ± 100. This compound was formulated as $[WCl_2(biphos)_2]^{2+}[WCl_6]^{2-}$. The far infrared bands at 316 cm^{-1} and 160 cm^{-1} were assigned to hexachlorotungstate(IV) anion and a band at 290 cm^{-1} was assigned to the cation. The magnetic moment was 1.69 B.M., a value lower than most reported tungsten(IV) complexes.

Converse (13) investigated the magnetic properties of $WCl_4[P(C_6H_5)_3]_2$ which he prepared by interaction of $P(C_6H_5)_3$ with $WCl_4(CH_3CH_2CN)_2$ in chloroform. He found a magnetic moment at room temperature of 2.00 B.M. and a linear relationship of χ'_M to temperature down to 77°K.

Butcher and Chatt (20) prepared a series of phosphine and arsine complexes by reaction of the desired ligand with $MoCl_4(CH_3CH_2CN)_2$ in dichloromethane at room temperature. The ligands for which crystalline complexes were isolated were diphenylethylphosphine, diethylphenylphosphine, diphenylmethylphosphine, diphenylpropylphosphine, diphos, cis-1,2-bis (diphenylphosphinoethene) and tripropylarsine. Diadducts were obtained with monodentate ligands and monoadducts with bidentates. The magnetic moment ranged from 2.18 to 2.61 B.M. The trans configuration was assigned to all but the complexes containing bidentate ligands. This assignment was made by comparison of the far infrared spectra with the spectrum of $MoCl_4$(biphos), a complex to which the cis configuration was assigned.

Allen, Feenan, and Fowles (15) also synthesized the molybdenum(IV) chloride triphenylphosphine and triphenylarsine adducts by dissolving $MoCl_4(CH_3CH_2CH_2CN)_2$ in chloroform along with excess ligand. The trans configuration was assigned to $MoCl_4[P(C_6H_5)_3]_2$ by comparison of the far infrared spectrum with that of $MoCl_4$(bipy), which was assumed to contain cis nitrogen atoms. The magnetic moments were 2.43 B.M. for

$MoCl_4[P(C_5H_6)_3]_2$ and 2.36 B.M. for $MoCl_4[As(C_5H_6)_3]_2$. The magnetic susceptibility of the triphenylphosphine complex was observed at four temperatures from 90°K to room temperature. A Curie-Weiss plot was linear, though a very small θ value was observed.

Oxygen and sulfur donors

Allen, Feenan, and Fowles (15) also prepared several complexes with oxygen donors by reaction of the ligand with $MoCl_4(CH_3CH_2CH_2CN)_2$ in chloroform. The monodentate ligands tetrahydrofuran, pentamethyleneoxide, and triphenylphosphine oxide were used. In all cases bis adducts were obtained. The magnetic moments ranged from 2.19 to 2.52 B.M. A thioxan (C_4H_8OS) diadduct was obtained by direct reaction of the ligand with $MoCl_4$. The C-O-C stretching frequency of this ligand was unchanged with coordination indicating coordination through the sulfur atom. No other complexes of sulfur donors have been reported.

A survey of the literature reveals that although a number of tungsten(IV) and molybdenum(IV) complexes have been prepared and magnetic data recorded, very little effort has been made to interpret the data. In most cases the authors quote room temperature magnetic moments and Curie-Weiss constants, but say little about what causes deviations from Curie behavior. Low moments were attributed to spin-orbit coupling effects without further comment on the reasons why strong spin-orbit coupling causes lowering. No studies have been made below liquid nitrogen temperature, even though the assumption that data taken at higher temperatures can be extrapolated to lower temperatures is often a faulty one.

Because of this situation, the aim of this study was to collect data for a number of complexes over a larger temperature range and suggest a model for explaining the behavior of the data. It is hoped that such a study will lead to more attempts to put the interpretation of the magnetic properties of d^2 systems on a sound basis.

EXPERIMENTAL

In this investigation the majority of the compounds prepared were susceptible to hydrolysis and air oxidation. All such compounds were handled and stored under vacuum or in an argon atmosphere dry box, maintained at a dew point of -75°. All liquid reactants and solvents were dried, stored in evacuated vessels, and transferred by vacuum distillation.

Materials

Metal

Tungsten powder was obtained from General Electric Refractory Metals Division. The metal was purified by passing a stream of hydrogen through it at 950° to remove any oxygen present. It was then stored in the dry box until it was used in a reaction.

Halogens

Lecture size cylinders of chlorine were utilized in metal halide syntheses. The chlorine was distilled into reaction vessels with a dry ice-acetone bath and thoroughly outgassed before use in a reaction.

Bromine was dried over phosphorus pentoxide, outgassed and distilled under vacuum into reaction vessels.

Organic reagents

Nitriles were dried by stirring over barium oxide, outgassing, and distillation onto Linde 4A Molecular Sieves which had been outgassed at 300° for twelve hours. They were stored over Molecular Sieves or niobium pentachloride. Spectrograde acetonitrile and reagent grade propionitrile and butyronitrile were used. Reagent grade pyridine was dried by outgassed Molecular Sieves. Lithium aluminum hydride was used to dry reagent grade sulfides. They were stored over the drying agent.

Spectrograde benzene was refluxed over sodium metal, outgassed and stored over niobium pentachloride. All other organic solvents were dried with molecular sieves. These included reagent grade dichloromethane and chlorobenzene and spectrograde chloroform.

Solid ligands such as 2,2'-bipyridine and triphenylphosphine were dried by thorough outgassing on a vacuum line.

Tungsten carbonyl

Tungsten carbonyl was purchased from Strem Chemical. It was stored in the dry box and outgassed under vacuum before use.

Analytical Methods

Samples for analysis were placed in screw cap vials in the dry box, weighed with the sample under argon, and transferred in the dry box to appropriate hydrolysis vessels. They were hydrolyzed with acid or base immediately upon removal from the dry box.

Tungsten

Tungsten was determined gravimetrically as the oxide, WO_3. Samples were weighed into tared crucibles, hydrolyzed with about 2 ml. of dilute nitric acid, and evaporated slowly to dryness. The residue was ignited in a muffle furnace for twelve hours at 550°. The samples were cooled in a desiccator before weighing.

Halogens

The samples were digested in a mixture of potassium hydroxide and hydrogen peroxide for several hours. When the sample was completely dissolved the solutions were cooled and brought to pH 1 with nitric acid. The halide was titrated potentiometrically with standard silver nitrate solution, using a pH meter equipped with silver and calomel electrodes.

The complexes $WCl_4(py)_2$ and $WCl_4(bipy)$ proved difficult to hydrolyze. The pyridine complex required treatment with a concentrated potassium hydroxide solution. This was evaporated to a small volume, about 5 ml., diluted to 50 ml. and a small amount of hydrogen peroxide added. The normal procedure was followed from this point. The bipyridine complex was hydrophobic and therefore was more readily hydrolyzed if it was dissolved in a small volume of ethanol before the base solution was added.

Carbon and hydrogen

Carbon and hydrogen were determined by Mr. John Richard of Ames Laboratory Analytical Service Group, Iowa State University.

Syntheses

Tungsten halides

Tungsten(VI) chloride was prepared by passing chlorine gas over tungsten metal at 550° for eight hours.

Tungsten(V) chloride was produced in two ways, by disproportionation of tungsten(IV) chloride,

$$3WCl_4 \rightarrow 2WCl_5 + WCl_2$$

and by reduction of tungsten(VI) chloride with tungsten carbonyl.

$$5WCl_6 + W(CO)_6 \rightarrow 6WCl_5 + 6CO$$

The disproportionation method involved placing a sealed tube containing tungsten(IV) chloride in a temperature gradient of 450° and 25° for 12 hours. The tungsten(V) chloride formed in the reaction sublimed to the cool end of the tube while WCl_2 remained in the hot region. Analytical, Calculated for WCl_5: Cl, 49.11; W, 50.89. Found: Cl, 48.67; W, 51.33. Cl/W = 4.91.

The difficulty in obtaining tungsten(IV) chloride made a new method desirable. The reduction of WCl_6 with $W(CO)_6$ proved to be a simple reaction which consistently gave high yields of WCl_5. A stoichiometric mixture of WCl_6 and $W(CO)_6$ were placed in a tube and heated to 100°. The tube was attached to a mercury bubbler to vent carbon monoxide given off by the reaction. Reaction was allowed to continue until evolution of gas ceased, usually 4 to 6 hours. Unreacted tungsten carbonyl was pumped out on the vacuum line. The product was then heated to 250° in a sealed tube to sublime it away from small amounts of WCl_4 produced in the reaction. Analytical. Cl, 47.92; W, 50.71; Cl/W = 4.90. The low Cl/W ratio was found to result from small amounts of $WOCl_4$ produced in the reaction. This could be removed by heating the pentahalide at 100° under vacuum to sublime out the oxyhalide.

Tungsten(IV) chloride was also prepared by employing several methods, reduction of WCl_6 with tungsten metal, reduction of WCl_6 with aluminum metal in aluminum chloride, and reduction of WCl_5 with tungsten carbonyl. The first two methods gave a brown solid which was very inert to reaction with most ligands. The third method gave a black powder which reacted relatively easily with organic ligands.

The reduction with tungsten metal was carried out in a sealed vycor tube in a temperature gradient of 675° and 300°C. Reaction was allowed to continue for four days. Product was deposited in the cool zone. Analytical. Calculated for WCl_4: Cl, 43.54; W, 56.46. Found: Cl, 38.02; W, 56.03; Cl/W = 3.51. Yields were good from this reaction but the product usually contained lower halide impurities.

The reduction with aluminum was carried out in a sealed tube in a temperature gradient of 250° and 230° using $AlCl_3$ as the solvent. The reaction took three to four days. Analytical. Found: Cl, 42.28; W, 57.95; Cl/W = 3.77. This reaction not only gave good yields but also a purer product. The length of time required for the reaction, and the difficulty in controlling the aluminum chloride pressures were disadvantages of this method.

The tungsten carbonyl reduction was done both dry and using chlorobenzene as a solvent. In the dry reaction, tungsten pentachloride and an excess of tungsten carbonyl were heated in a tube under argon. The carbon monoxide was vented through a mercury bubbler. The solids were heated at 140° to 160° until evolution of carbon monoxide ceased. Alternatively, excess tungsten pentachloride and a slight deficiency of tungsten carbonyl were mixed in chlorobenzene. A water cooled condensor was used to prevent solvent loss and a mercury bubbler to prevent CO pressure buildup. The system was pressurized to one atmosphere with argon and the solution refluxed at 130° to 140° until carbon monoxide evolution ceased.

The product from the reaction, whether done dry or in solvent, was transferred to a tube and heated at 225° to sublime unreacted WCl_5 and volatile oxyhalide impurities. The yield was 50 to 60% with no solvent and 80 to 90% in solvent. The yield was reduced with no solvent because of the volatility of tungsten carbonyl. Analytical (reaction without solvent).

Found: Cl, 43.25; W, 56.47; Cl/W = 3.97. Reaction in chlorobenzene. Found: Cl, 44.09; W, 55.99; Cl/W = 4.08.

The same conditions were utilized to react WCl_6 with $W(CO)_6$ in an attempt to obtain tungsten(IV) chloride directly from WCl_6. The yield was approximately 50% WCl_4 and 50% WCl_5. The product obtained was not as pure as the product obtained when WCl_5 was the initial reactant. Analytical. Found: Cl, 41.52; W, 57.53; Cl/W = 3.74.

Tungsten(V) bromide was synthesized by passing bromine over tungsten metal at 650° for several days. The product was resublimed at 300° to decompose any WBr_6 formed.

Tungsten carbonyl when reacted with tungsten(V) bromide gave the lower halide WBr_4. The temperature necessary for this reaction was 180 to 200°. Because of the high volatility of tungsten carbonyl at these temperatures the reaction was performed by placing the reactants in a Pyrex tube with a Teflon cap which was held on loosely with springs. This also served as a pressure release for the tube. The reaction tube was placed in a stainless steel bomb under 1 atmosphere of argon. The bomb was heated to 180° for 12 hours. The bomb was then evacuated and the product removed in the dry box. The product was heated under vacuum to 250° to remove unreacted carbonyl and pentahalide. Yield was about 50%. Analytical. Calculated for WBr_4: Br, 63.48; W, 36.52. Found: Br, 62.84; W, 36.51; Br/W = 3.95.

Complexes of sulfur donors

Ethyl sulfide was found to react directly with tungsten (IV) chloride which was obtained by the tungsten carbonyl reduction of tungsten(V) chloride. The halide was stirred for 12 hours in the neat ligand at 50°-60°. The product was extracted away from unreacted WCl_4 with dichloromethane or benzene. A red-orange crystalline solid was obtained. The product was soluble in chloroform, dichloromethane, benzene, toluene and ethyl sulfide. Analytical. Calculated for $WCl_4[(C_2H_5)_2S]_2$: Cl, 28.04; W, 36.37. Found: Cl, 28.13; W, 36.45; Cl/W = 4.01.

The tetrahydrothiophene adduct was prepared by continual extraction of WCl_4 with the ligand. About 2 grams of the red crystalline product were obtained after several days of extraction. The compound was only sparingly soluble in organic solvents but had a solubility of approximately .001M in the ligand. Analytical. Calculated for $WCl_4(C_4H_8S)_2$: Cl, 28.26; W, 36.66; C, 19.12; H, 3.19. Found: Cl, 28.02; W, 36.48; C, 19.44; H, 3.05; Cl/W = 3.99.

Attempts were made to obtain the analogous bromide complexes WBr_4L_2 by reaction of WBr_4 with the ligands. With both ethyl sulfide and tetrahydrothiophene, the products were oily solids which proved difficult to dry. Analysis gave low bromide to tungsten ratios, probably indicating partial reduction of the metal by the ligand. Analytical. Calculated for

$WBr_4[(C_2H_5)_2S]_2$: Br, 46.73; W, 26.89. Found: Br, 45.86; W, 27.80; Br/W = 3.80. Calculated for $WBr_4(C_4H_8S)_2$: Br, 47.01; W, 27.05. Found: Br, 42.91; W, 27.41; Br/W = 3.65.

Reaction of $WBr_4(CH_3CN)_2$ with ethyl sulfide gave a brown solid. The infrared spectrum indicated no acetonitrile remained in the complex. Analytical: Br, 52.38; W, 33.92; Br/W = 3.56; Et_2S/W = .82.

Complexes of nitrile donors

The nitrile complexes, $WCl_4(RCN)_2$ were synthesized by employing several methods. These included direct reaction with WCl_4, reduction of WCl_5 by the ligand, and reduction of WCl_5 with another reducing agent in the ligand.

The acetonitrile complex $WCl_4(CH_3CN)_2$ was prepared using all of these methods. Direct reaction of WCl_4 with acetonitrile proceeded at 50°C. The reaction was quite slow (several days were needed to obtain over 1 gram of product). Since $WCl_4(CH_3CN)_2$ was insoluble in common organic solvents it was not possible to remove unreacted WCl_4 from the final product. The reaction of WCl_5 with acetonitrile gave 50 to 60% yield of $WCl_4(CH_3CN)_2$ in 1 to 2 hours. The product was purified by washing with acetonitrile. The product obtained from the reaction often had a low chlorine to tungsten ratio and contained organic oxidation products which were difficult to remove. Adding zinc to the reaction as a reducing agent increased neither the yield nor the quality of the product.

The method which consistently gave the best product and yield was reduction of WCl_5 with $W(CO)_6$ in acetonitrile.

$$4WCl_5 + W(CO)_6 + 10CH_3CN \rightarrow 5WCl_4(CH_3CN)_2 + 6CO$$

This reaction proceeded at room temperature with evolution of carbon monoxide. A stoichiometric mixture of the reactants was stirred in excess acetonitrile for 12 hours. The product was extracted with acetonitrile to remove soluble side products and unreacted $W(CO)_6$. About 60 to 70% yields of $WCl_4(CH_3CN)_2$ were recovered. Analytical. Calculated for $WCl_4(CH_3CN)_2$: W, 45.09; Cl, 34.77. Found: W, 45.26; Cl, 34.82; Cl/W = 3.99.

The propionitrile complex $WCl_4(CH_3CH_2CN)_2$ was most easily prepared by direct reaction of the ligand with WCl_4. Reactants were stirred at 50°C for 24 hours. The complex was soluble enough in propionitrile to extract it away from unreacted tetrachloride. Analytical. Calculated for $WCl_4(CH_3CH_2CN)_2$: Cl, 32.55; W, 42.21. Found: Cl, 32.26; W, 42.38.

Reaction of $WCl_4(CH_3CN)_2$ with propionitrile also gave $WCl_4(CH_3CH_2CN)_2$ in good yield. Reduction reactions did not give a pure product because of difficulties in removing organic oxidation products. Such reactions also tended to give products with low halide to metal ratios.

The butyronitrile complex, $WCl_4(CH_3CH_2CH_2CN)_2$, in particular presented synthetic problems. It was impossible to separate the pure complex from the products obtained by reaction of WCl_5 with butyronitrile. Direct reaction of WCl_4 with butyronitrile proceeded at 60 to 70°. The product could be extracted away from unreacted WCl_4 with butyronitrile. The red complex was crystallized out of butyronitrile. The same compound could be obtained by stirring $WCl_4(CH_3CN)_2$ in butyronitrile at 40 to 50°C. The product from these methods gave analytical data which indicated that the chloride to tungsten ratios were near four, however, the ligand to metal ratios were often slightly high, 2.1 to 2.2. This was perhaps due to excess solvent being carried down in the crystallization process.

This problem was avoided when the complex was prepared by reacting excess $WCl_4[(C_2H_5)_2S]_2$ and a deficiency of butyronitrile in dichloromethane. The butyronitrile complex separated from the dichloromethane solution in crystalline form. Unreacted $WCl_4[(C_2H_5)_2S]_2$ was easily extracted from the product with dichloromethane. A yield of 80 to 90% was obtained. Calculated for $WCl_4(CH_3CH_2CH_2CN)_2$: Cl, 30.57; W, 39.63. Found: Cl, 30.57; W, 39.45; Cl/W = 4.01.

The butyronitrile complex was soluble in benzene and butyronitrile, but only slightly soluble in chloroform and dichloromethane. The solution spectrum in the near infrared region (8000 to 15000Å) was recorded in butyronitrile and in benzene on the Cary 14 spectrophotometer in a quartz cell. The spectra were identical in both solvents. Extinction coefficients of the bands were determined in benzene (molar extinction coefficients are given in parenthesis) 14,800Å (7.5); 14,400 (8.0); 13,950 (10.4); 13,400 (6.0); 12,250 (4.0); 10,150 (5.5); 9,900 (7.2); 8,150 (9.2).

The solution spectrum was quite complex. Without further study no assignment of these bands can be made.

The bromide nitrile adducts $WBr_4(RCN)_2$ were found to be more stable than the sulfide adducts. The complex $WBr_4(CH_3CN)_2$ was obtained in 50% yield by reduction of WBr_5 with acetonitrile. The product, an insoluble brown solid, was separated from the impurities by washing with acetonitrile. Analytical. Calculated for $WBr_4(CH_3CN)_2$: Br, 54.59; W, 31.40; C, 8.20; H, 1.02. Found: Br, 54.77; W, 31.20; C, 8.49; H, 1.08; Br/W = 4.04.

Another method which proved useful in obtaining the same product was the reaction of tungsten carbonyl with bromine in acetonitrile. The reaction proceeded readily at room temperature with vigorous evolution of carbon monoxide. A subsequent extraction with acetonitrile removed side products. The yield of $WBr_4(CH_3CN)_2$ was 70 to 80%. This method had the advantage of utilizing readily available starting reactants. Analytical. Found: Br, 54.73; W, 31.28; Br/W = 4.03. The infrared spectrum of the other products of the above reaction, those which were soluble in acetonitrile, was recorded. It indicated a small amount of coordinated acetonitrile and appreciable amounts of carbonyl present.

The propionitrile and butyronitrile adducts of tungsten tetrabromide were prepared by reaction of the acetonitrile complex $WBr_4(CH_3CN)_2$ with the appropriate ligand. The complex $WBr_4(CH_3CH_2CH_2CN)_2$ was a black crystalline solid as recovered from butyronitrile.

It exhibited a high ligand to metal ratio even though the bromide to metal ratio was near four. Analytical. Calculated for $WBr_4(CH_3CH_2CH_2CN)_2$: Br, 49.82; W, 28.60. Found: Br, 49.02; W, 28.75; Br/W = 3.93; butyronitrile/W = 2.15.

Complexes of pyridine and bipyridine

Stirring tungsten(IV) chloride with pyridine for several days at 60° yielded the complex $WCl_4(py)_2$. The complex was an insoluble salmon-colored powder. However, the product obtained by this method was often contaminated by small amounts of unreacted WCl_4.

The complex was also synthesized by reaction of $WCl_4[(C_2H_5)_2S]_2$ with a slight deficiency of pyridine in benzene. The reaction time was 10 minutes at room temperature. Unreacted ethyl sulfide complex was washed away with benzene. Analytical. Calculated for $WCl_4(C_5H_5N)_2$: Cl, 29.33; W, 37.99. Found: Cl, 28.95; W, 37.64; Cl/W = 3.99.

When a solution of $WCl_4(CH_3CH_2CH_2CN)_2$ in benzene or butyronitrile was mixed with a slight excess of pyridine a brown solid precipitated. When the product was washed with benzene, part was extracted and part remained undissolved. The amount of the soluble portion varied from 50 to 90% of the total product. Analysis of the soluble portion indicated a stoichiometry, $WCl_4(py)_2$. Calculated for $WCl_4(C_5H_5N)_2$: Cl, 29.33; W, 37.99. Found: Cl, 29.42; W, 38.07; Cl/W = 4.01. The insoluble portion had a chloride to tungsten ratio of about 4.2. Found: W, 34.69; Cl, 28.10.

The complex, WCl_4(bipy), was also obtained by direct reaction of excess 2,2'-bipyridine with tungsten(IV) chloride in benzene. For the reaction to go to completion stirring for 5 to 6 days at 60° was required. Analytical. Calculated for $WCl_4(C_{10}H_8N_2)$: Cl, 29.43; W, 38.17; C, 24.91; H, 1.68. Found: Cl, 29.91; W, 38.54; C, 25.29; H, 1.70; Cl/W = 4.02.

The complex, a brick red solid which was insoluble in most organic solvents, was prepared more readily by stirring $WCl_4[(C_2H_5)_2S]_2$ with a slight excess of 2,2'- bipyridine at room temperature for several hours. An extraction with benzene removed unreacted bipyridine. An analogous reaction starting with $WCl_4(CH_3CH_2CH_2CN)_2$ instead of $WCl_4[(C_2H_5)_2S]_2$ did not give a pure product.

A complex of triphenylphosphine

The same method, $WCl_4[(C_2H_5)_2S]_2$ mixed with a slight excess of ligand in chloroform, was used to synthesize $WCl_4[P(C_6H_5)_3]_2$. Unreacted ligand was removed by washing with chloroform. The complex was an air stable yellow solid which was insoluble in organic solvents. Calculated for $WCl_4[P(C_6H_5)_3]_2$: Cl, 16.68; C, 50.86. Found: Cl, 16.59; C, 50.70.

Physical Measurements

Infrared spectra

Infrared spectra were recorded on the Beckman IR-7 (600 to 4000 cm^{-1}) and the Beckman IR-11 (90 to 800 cm^{-1}) spectrophotometers. Samples were prepared by grinding and mulling with Nujol. For the IR-7 mulls were placed between cesium iodide or sodium chloride windows. The windows were sealed with a thin film of vaseline around the edges. For the IR-11 mulls were placed between polyethylene sheets. These were sealed by an O-ring in the window holder.

Infrared spectra were taken at low temperatures in the region 200 to 800 cm^{-1} on the Beckman IR-11 by using a specially designed cell. The cell consisted of a liquid nitrogen reservoir in contact with a copper window holder which contained a cesium iodide window. The reservoir fit into an outer jacket which was equipped with two cesium iodide windows. These lined up with the inner window to give an unobstructed beam path. A mull was placed on the inner window in the dry box. The cell was removed and evacuated through a Teflon stopcock in the outer jacket. This formed a vacuum jacketed space for the reservoir and protected the sample from hydrolysis and air oxidation.

Solution spectra in the region 90 to 600 cm^{-1} were taken in polyethylene cells with a 0.1 or 0.2 mm. path length. Solutions were made up and transferred to the cells in an argon atmosphere dry box. The cells were sealed by melting the polyethylene neck on the cells with a soldering gun.

Nuclear magnetic resonance spectra

Nuclear magnetic resonance spectra were obtained on the Varian A-60, Varian HA-100, and Hitachi Perkin-Elmer R-20B Spectrometers. The R-20B was equipped with a variable temperature controller which performed over the range of +100° to -100°. Solutions were made up on the vacuum line, filtered into a n.m.r. tube and sealed off under vacuum. Tetramethylsilane was distilled in as an internal standard when needed.

X-ray powder patterns

Samples for powder patterns were sealed into 0.2 or 0.5 mm. Lindemann capillary tubes. A 114.59 mm. Debye-Scherrer camera was used. The samples were exposed to copper Kα radiation for 12 to 18 hours.

Magnetic susceptibility

Magnetic susceptibility measurements were made on a Faraday balance. The construction and calibration of the balance were discussed in detail by Converse (13). A cryostat was added to the balance to allow cooling of the sample with liquid nitrogen or liquid helium. When liquid helium was placed in the cryostat the lowest sample temperature equilibrated at 19° to 20°K. A heater and automatic temperature controller were contained in the system. Temperature controlling was done with a copper/gold-2.1% cobalt thermocouple. Sample temperature was read with a copper-constantan thermocouple in the range 40 to 300°K, and with a copper/gold-0.07% iron thermocouple from 20° to 50°K. Temperatures could be controlled and read to ± 0.5°K except from 35 to 45°K. In this range emf changes were small for both thermocouples so temperature readings were only good to ± 2°K. Thermocouples were calibrated by Mr. John Greiner of Ames Laboratory, Iowa State University.

Samples were prepared by placing about 100 mg. of solid in a small Teflon bucket in the dry box. Samples were kept under argon until they could be placed in the balance and the chamber evacuated.

Electron spin resonance

Electron spin resonance data were recorded by Dr. William Antholine on a Strand 602B, x-band spectrometer. Samples were sealed in quartz tubes for the measurements.

RESULTS AND DISCUSSION

Characterization of Tungsten(IV) Chloride

The preparation of WCl_4 by reduction of WCl_5 with $W(CO)_6$ was described in the previous section. It was noted that the product obtained by this method differed from the product obtained from other methods in its reactivity toward organic ligands. For example, the WCl_4 prepared by reduction with tungsten or aluminum metal did not react with nitriles, even with extensive refluxing; however, the WCl_4 prepared by reduction with $W(CO)_6$ reacted with nitriles at 50° to give bis-adducts $WCl_4(RCN)_2$.

Because of these differences, several of the physical properties of this halide were studied and compared with the properties of the halide prepared by other methods. To differentiate between the two forms we shall call the product obtained by reduction with tungsten or aluminum α-WCl_4 and the product obtained by reduction with $W(CO)_6$, β-WCl_4.

The X-ray powder diffraction data for α-WCl_4 were reported by T. M. Brown (11). These are compared with the corresponding data for β-WCl_4 in Table 1.

Though there are a number of coincident lines in the patterns there are an equal number of noncoincident lines. Thus the two compounds are indicated to have similar structures, but belong to different crystal types.

The infrared spectrum of β-WCl_4 was also compared with

Table 1. X-ray powder diffraction data for α-WCl_4 and β-WCl_4

α-WCl_4	β-WCl_4	α-WCl_4	β-WCl_4
	6.62^{a}vs^b	2.18 vvs	
5.97^{a}vvs^b	5.96 vvs	2.13 vw	
	5.31 vs	2.10 w	2.11s
4.45 vvs	4.80 vw	2.02 s	
4.02 vvs	3.94 vs	2.00 w	
	3.77 vvs	1.98 vvw	1.98 vw
	3.34 vw	1.93 vvw	1.93 vvw
3.23 vs	3.21 vvs	1.86 vvw	
3.03 vvw		1.84 vvw	
2.85 vw	2.83 w	1.81 vvw	1.81 vvw
2.77 w	2.71 w	1.76 vvw	1.76 vvw
2.62 vs	2.67 w	1.73 vvw	
2.58 s	2.56 w	1.71 vw	1.71 s
2.54 w	2.33 s	1.68 vvw	1.66 vvw
2.23 s	2.27 s	1.61 vw	1.61 vw
	2.25 w	1.59 vw	1.55 vvw

^{a}d-spacings in A.

^{b}v = very, w = weak, s = strong.

the spectrum of α-WCl_4 as determined by R. Hogue (21). These data are given in Table 2. The abbreviations given here for intensity and line width are those used in all subsequent tables.

The spectra of the two complexes were very similar. The main differences were in intensity and resolution of the bands. The strong bands near 250 cm^{-1} in both forms are indicative of bridging halogens (22).

The magnetic susceptibility of α-WCl_4 was measured by McCarley and Brown (10). The complex was diamagnetic with

Table 2. Far infrared spectra of α-WCl_4 and β-WCl_4

α-WCl_4	β-WCl_4
122^{a}s,sh^b	124^{a}s,sh^b
164 s, sh	168 s, sh
	229 m, sh
240 vs, br	250 s, br
289 m, sh	289 w, br
357 vs, br	365 vs, sh
387 s, br	

[a] Absorption maxima in cm^{-1}.

[b] s = strong, m = medium, w = weak, br = broad, sh = sharp v = very.

$\chi_M = -58x10^{-6}$ at room temperature. The magnetic susceptibility of β-WCl_4 was measured at a number of temperatures from that of liquid nitrogen to room temperature (Table 3).

Table 3. Magnetic susceptibility of β-WCl_4

Temperature °K	$\chi_g(10^6)$ emu/gram	$\chi_M(10^6)$ emu/mole
296	-0.146	-47.7 ± .2
147	-0.150	-48.8 ± .1
126	-0.153	-49.8 ± .1
108	-0.152	-49.5 ± .2
85	-0.140	-45.8 ± .7
Average values	-0.148	-48.3 ± 1.3

Sample mass 0.1495 g; molecular weight 325.7 g/mole

The lack of temperature dependence of the values indicated the complex was relatively free of paramagnetic impurities. As in the case of α-WCl_4 the diamagnetism of β-WCl_4 indicates that metal-metal bonding may be an important structural feature of this lower halide.

The near infrared spectrum (600-4000 cm^{-1}) of β-WCl_4 was recorded to find if any carbonyl or oxyhalide impurities were detectable. However, no bands were seen over this region.

Examination of the physical properties of both forms of WCl_4 indicated that the difference was mainly the variation in the X-ray powder pattern. This may indicate that the two forms are simply variations of the same structure.

Characterization of Tungsten(IV) Halide Adducts

A method which has often been used to aid in assigning stereochemistry of _cis_ and _trans_ octahedral complexes is a study of metal-halogen stretching frequencies in the far infrared region (22). For _trans_ complexes (D_{4h}), group theory predicts one infrared active metal-halogen stretching frequency (e_u) and for _cis_ it predicts four ($2a_1+b_1+b_2$). If more than one band can be assigned as a metal-halogen stretching frequency, a _cis_ configuration can be assigned with some confidence. However, if only one broad band is seen it may be due to a lack of resolution, so it is more difficult to feel confident in a _trans_ assignment.

Nitrile complexes

The infrared spectra in the region 90-4000 cm^{-1} of the nitrile complexes $WBr_4(CH_3CN)_2$ and $WCl_4(RCN)_2$, (R = CH_3, C_2H_5, C_3H_7) are given in Tables 1A-4A. The far infrared spectra at low temperatures are also recorded.

The near IR spectra of the complexes show the rise in frequency of the carbon-nitrogen stretching frequency which is characteristic of nitriles coordinated through the nitrogen atom (23).

The bands which fall in the region where metal-halogen stretching frequencies usually occur, 200-500 cm^{-1}, are recorded in Table 4.

In the chloro complexes only one broad band can be assigned to the metal-chloride stretching frequency at room temperature; however, in both complexes this band splits at low temperature. In the bromo complex two metal-bromide stretching frequencies are seen at room temperature. These are resolved into three bands at low temperature. The band at 284 cm^{-1} in $WCl_4(CH_3CN)_2$ may be a metal-halogen stretching frequency; but, since there is a band at nearly the same frequency in $WBr_4(CH_3CN)_2$, it is more likely a metal-ligand stretching or bending mode. The splitting of the metal-halogen stretching frequencies at low temperature in the bromide and chloride acetonitrile complexes is illustrated in Figure 1. Since more than one metal-halogen stretching frequency is

Table 4. Far infrared spectra of acetonitrile and propionitrile complexes (200-500 cm^{-1})

	$WCl_4(CH_3CN)_2$	
$\nu(cm^{-1})^a$		$\nu(cm^{-1})^b$
235 s,sh 284 m,sh	unassigned	237 m,sh 245 w,br 289 m,sh
325 vs,vbr	W-Cl stretch	320 s,br 337 s,br
418 m,sh 428 m,sh	C-C≡N bend	425 m,sh 435 m,sh
	$WBr_4(CH_3CN)_2$	
$\nu(cm^{-1})^a$		$\nu(cm^{-1})^b$
216 vs,br 245 vs,br	W-Br stretch	218 vs,sh 242 vs, sh 250 vs,sh
283 m,sh	unassigned	287 w,br
425 m,sh 435 m,sh	C-C≡N	426 m,sh 436 m,sh
	$WCl_4(CH_3CH_2CN)_2$	
$\nu(cm^{-1})^a$		$\nu(cm^{-1})^b$
265 m,br	unassigned	268 w,br
330 vs,vbr	W-Cl stretch	327 s,br 345 s,br
426 m,sh	ligand bend	428 w,sh

[a] Room temperature.

[b] Low temperature.

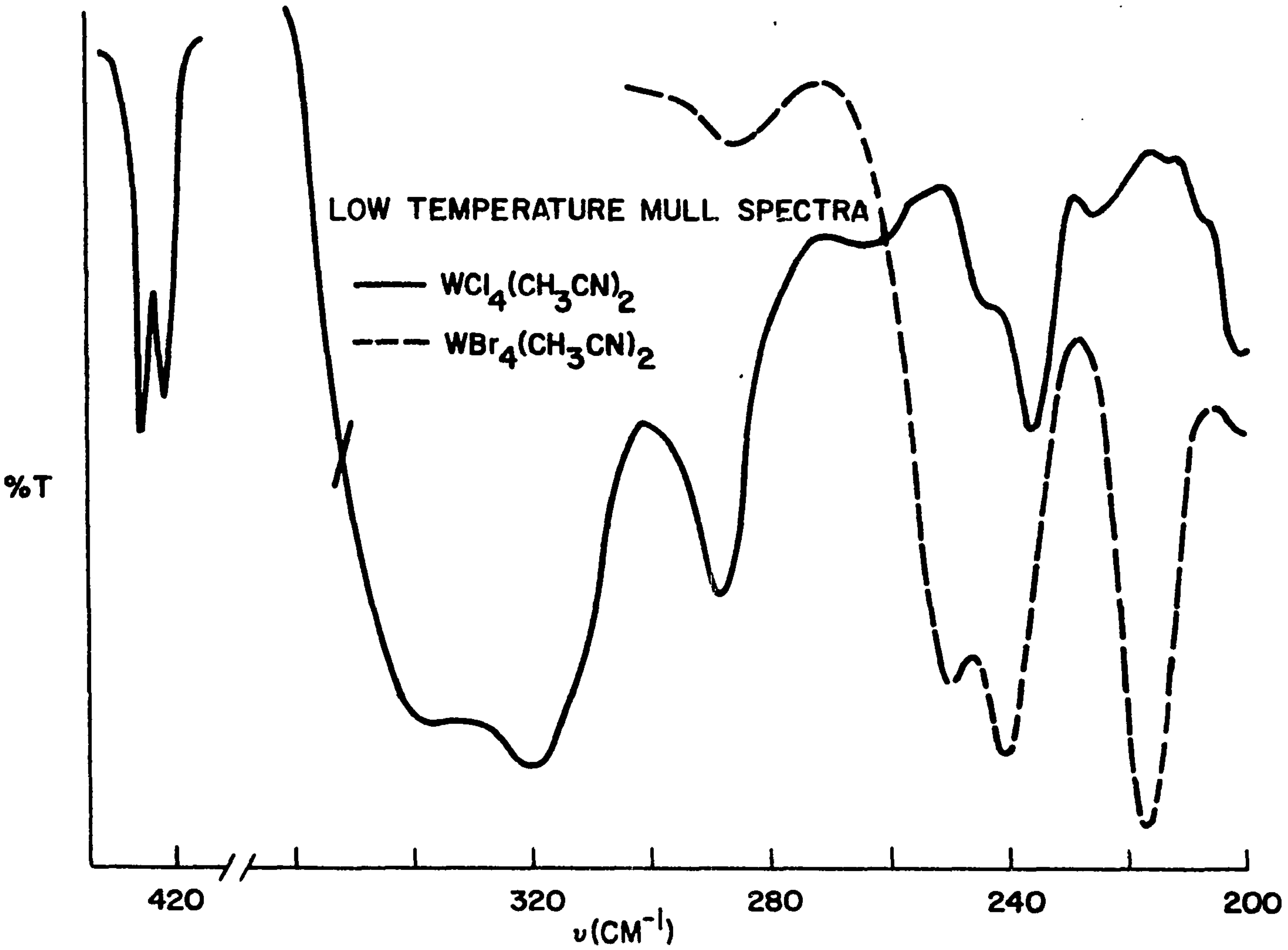

Figure 1. Far infrared spectra of acetonitrile adducts

observed these complexes are assigned a <u>cis</u> configuration.

Assignment of the configuration of the butyronitrile complex proved more difficult than the other nitrile complexes. The spectrum from 200-500 cm^{-1} is given in Table 5.

Table 5. Far infrared spectrum of $WCl_4(CH_3CH_2CH_2CN)_2$

(cm^{-1})^a		(cm^{-1})^b
264 w, br	Unassigned	264 w, br
330 vs, br	W-Cl stretch	330 vs, vbr
395 m, sh		393 s, sh
426 m, sh	Ligand bend	425 s, sh

^{a}Room temperature.

^{b}Low temperature.

The spectrum showed very little change with temperature. The single metal-chloride stretching frequency, which was very broad at room temperature, remained broad but did not split at low temperature. The spectrum of a solution of the complex in benzene was also recorded over this region. This spectrum had a strong sharp band at 330 cm^{-1} which was assigned to the metal-chloride stretching frequency. The room temperature, low temperature, and solution spectra are compared in Figure 2. The complex is tentatively assigned the <u>trans</u> configuration. This assignment is reasonably certain for benzene solutions but not as certain for the solid state. The broadening of the W-Cl stretching band in the solid state

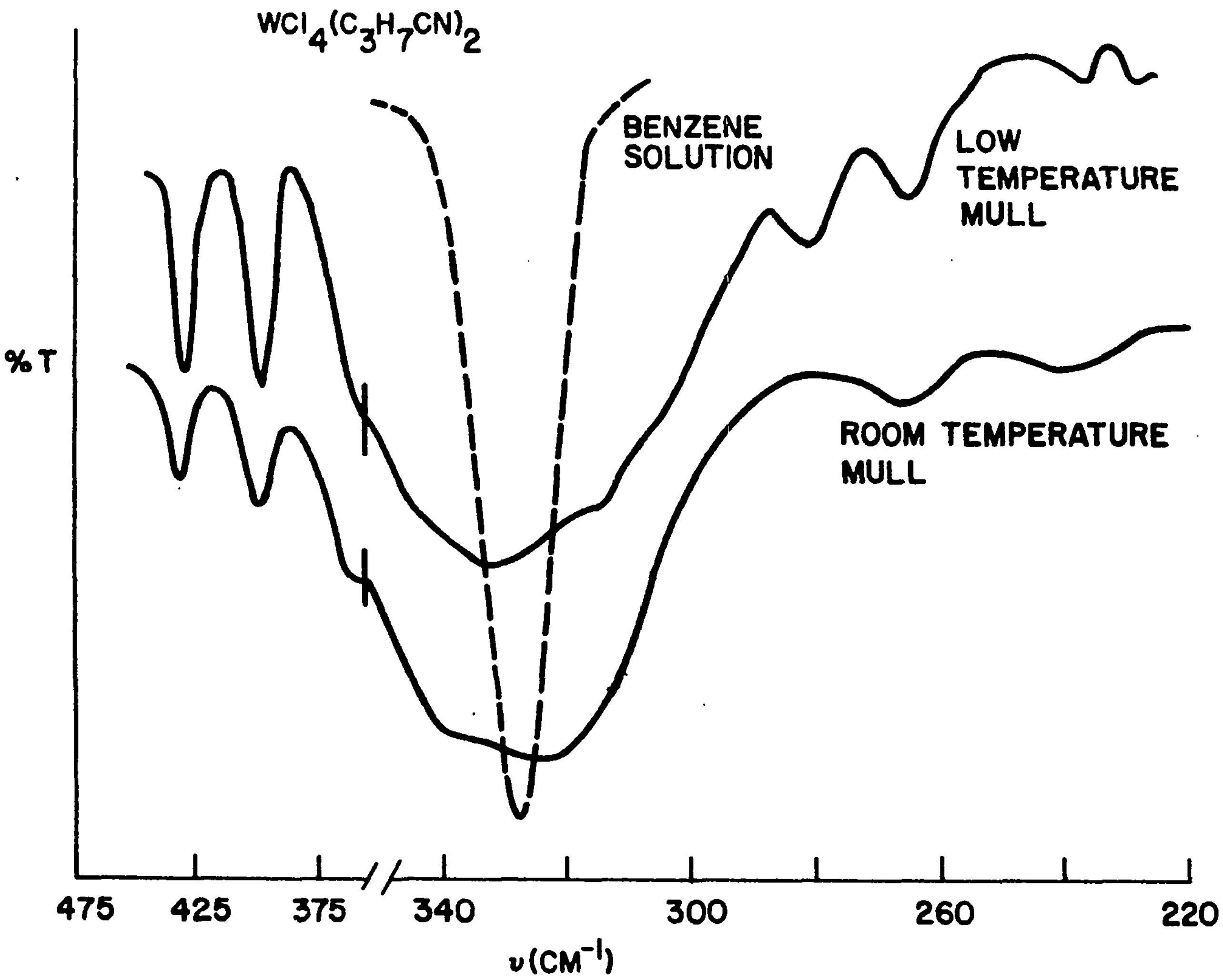

Figure 2. Far infrared spectrum of $WCl_4(C_3H_7CN)_2$

spectrum may be due to lack of symmetry in the crystal lattice.

An attempt was made to measure the dipole moment of $WCl_4(CH_3CH_2CH_2CN)_2$ in benzene. A zero or near zero value of dipole moment would be expected for a _trans_ complex and a high moment for a _cis_ complex. (The moment of _cis_ $TiCl_4(CH_3CH_2CN)_2$ is 7.74 and that of _cis_ $TiCl_4(CH_3CN)_2$ is 7.97D. at room temperature) (24). The value found was 2.47 Debye. Difficulties were encountered, however, in making the measurement. The solutions were extremely sensitive to hydrolysis and some reaction with impurities in the cell appeared to take place. This was possibly the cause of the intermediate value. Another possibility is a _cis_-_trans_ isomerism in benzene. The infrared spectrum in benzene, however, does indicate that the _trans_ form is definitely favored in that solvent.

The infrared spectra of the sulfide adducts $WCl_4[C_2H_5)_2S]_2$ and $WCl_4(C_4H_8S)_2$ are recorded in Tables 5A and 6A. The near infrared spectra show the bands characteristic of the ligands. Tetrahydrothiophene has a band at 685 cm^{-1} which has been assigned to a ring stretching mode (25). This band is characteristically shifted to lower frequencies on coordination of the ligand. In this complex the band is observed at 663 cm^{-1}, a shift downward of 22 cm^{-1}.

The far infrared spectra of these sulfide complexes in the metal-halogen stretching region are given in Table 6.

Both complexes had a single metal-halogen stretching

Table 6. Far infrared spectra of sulfide complexes (200-500 cm^{-1})

$WCl_4[(C_2H_5)_2S]_2$

	(cm^{-1})^a	(cm^{-1})^b	(cm^{-1})^c
Unassigned	260 vw,br 275 vw,br	275 w,br	272 m,br
W-Cl stretch	330 vs,vbr	325 vs,vbr	326 vs,vbr
Ligand band	395 w,m	395 wsh	395 wsh

$WCl_4(C_4H_8)_2$

	(cm^{-1})^d	(cm^{-1})^b	(cm^{-1})^c
Unassigned	264 w,br	262 s,vbr	256 msh 272 msh
W-Cl stretch	327 ssh	325 vs,vbr	323 s,br
Ligand band	480 msh	472 msh	475 msh

[a] Solution in benzene.

[b] Room temperature.

[c] Low temperature.

[d] Solution in tetrahydrothiophene.

frequency at room temperature. The effect of going to low temperature contrasted sharply. For the ethyl sulfide complex the metal-chloride stretching frequency was unaffected by the change in temperature, while the tungsten-chloride stretching frequency in the tetrahydrothiophene complex narrowed from a line width of 30 cm^{-1} to one of 20 cm^{-1}. In solution the effect was similar. The tungsten-chloride stretching frequency of $WCl_4[(C_2H_5)_2S]_2$ in benzene was broad and structured just as it was in the solid, while the band in $WCl_4(C_4H_8S)_2$ became sharp in a tetrahydrothiophene solution (Figure 3). Because of these observations, the ethyl sulfide complex was assigned the cis configuration and the tetrahydrothiophene complex the trans configuration. The reason for this difference is hard to understand when the similarity of the two ligands is considered.

The infrared spectrum (90-4000 cm^{-1}) of $WCl_4[P(C_6H_5)_3]_2$ is recorded in Table 7A. The far infrared spectrum from 200-500 cm^{-1} is given in Table 7.

Table 7. Far infrared spectrum of $WCl_4[P(C_6H_5)_3]_2$ (200-500 cm^{-1})

$(cm^{-1})^a$		$(cm^{-1})^b$
257 w,br	Unassigned	258 vw,br
		279 w,br
322 s,br	W-Cl stretch	322 s,br
436 m,sh		430 w,br
454 m,sh	Ligand	455 s,sh
499 s,sh	bands	496 s,sh

[a] Room temperature.

[b] Low temperature.

A single tungsten-chloride stretching frequency was observed in this complex. The band failed to split at low temperature, and changed very little in line width, as shown in Figure 4. Because of the sharpness of this band a trans configuration was assigned to $WCl_4[(C_6H_5)_3P]_2$.

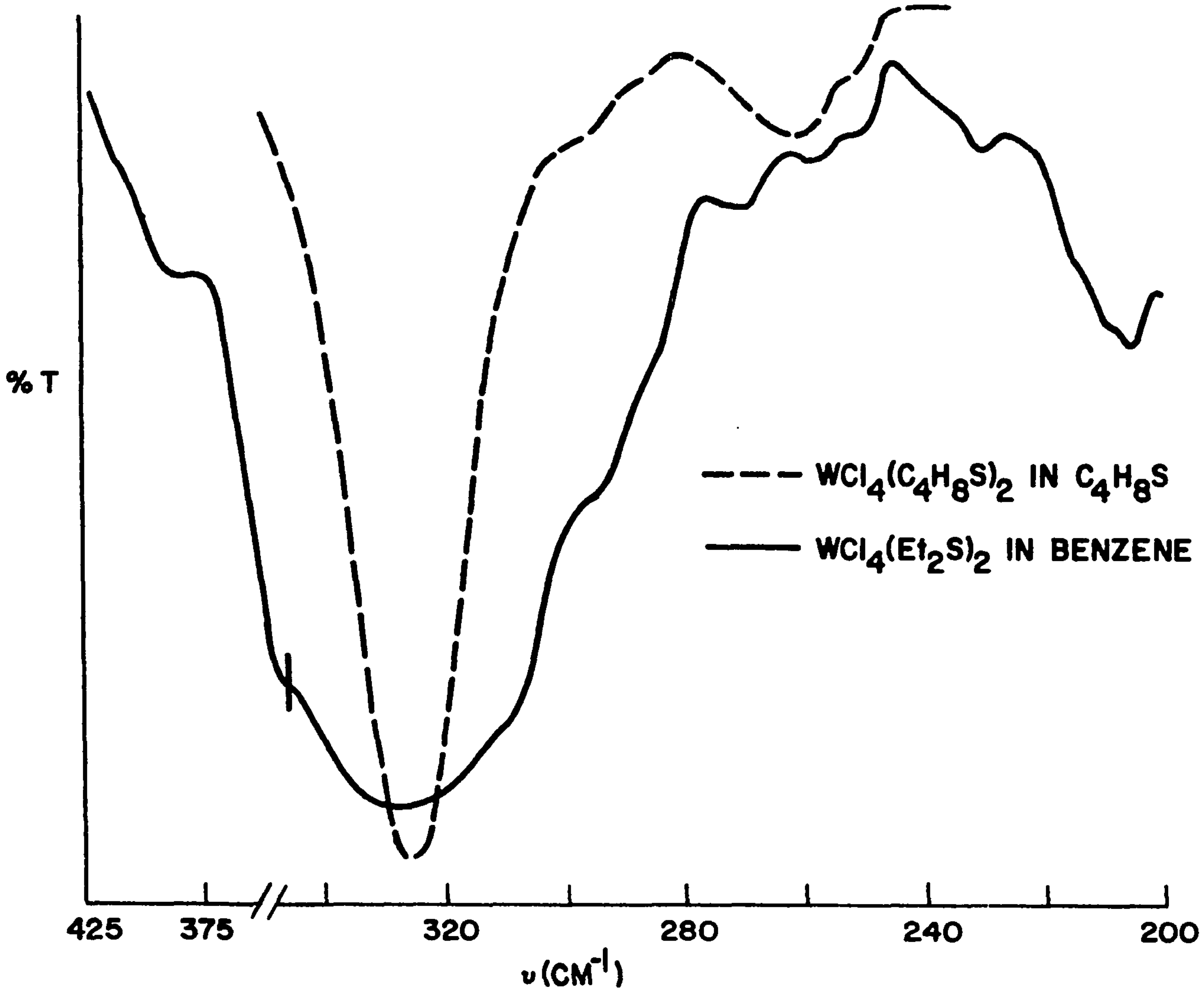

Figure 3. Far infrared spectra of sulfide adducts in solution

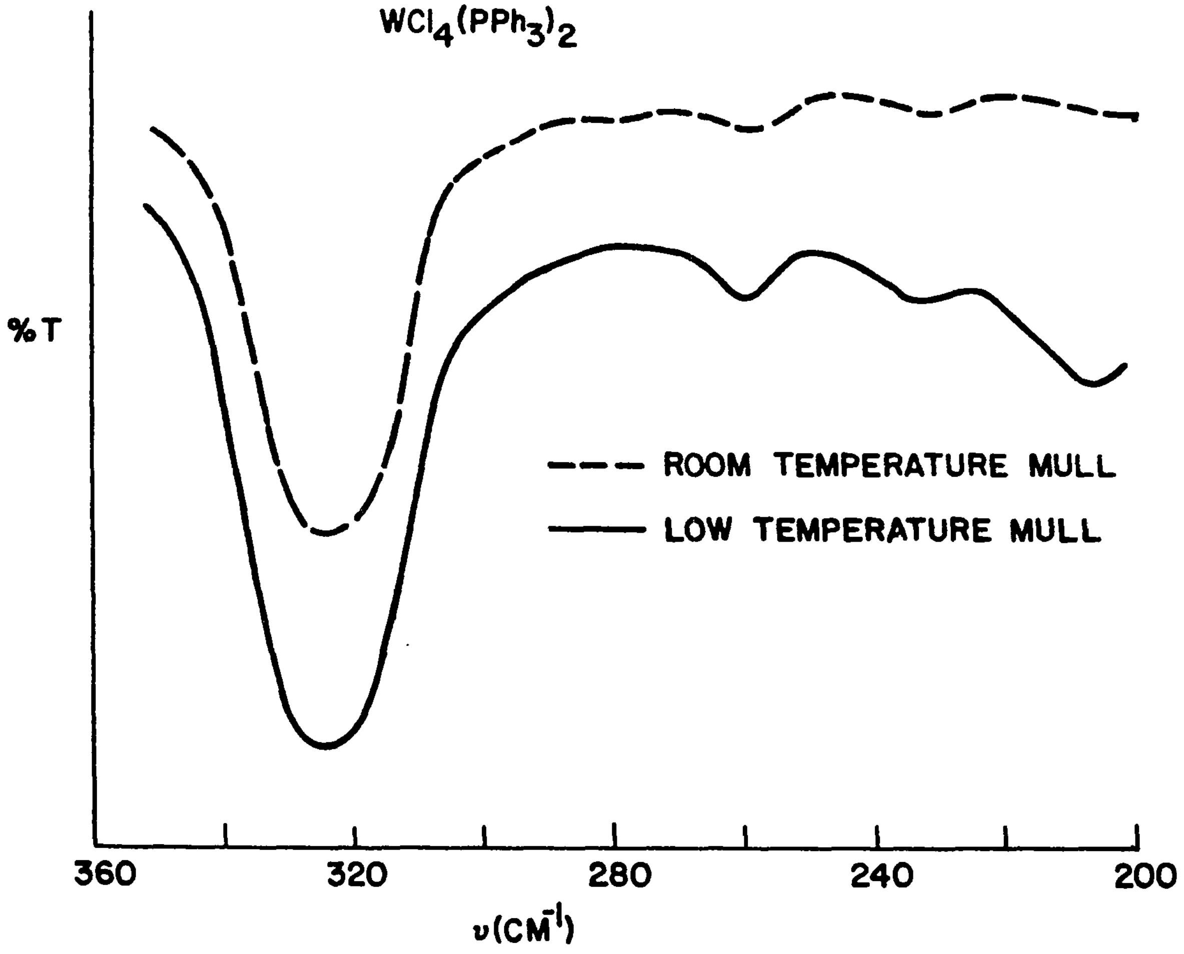

Figure 4. Far infrared spectrum of $WCl_4[(C_6H_5)_3P]_2$

Two methods for preparing pyridine adducts were described in the experimental section. The first was reaction of $WCl_4[(C_2H_5)_2S]_2$ with pyridine in benzene, a reaction which yielded a single insoluble product. This product will subsequently be referred to as $WCl_4(C_5H_5N)_2$(I). The second method was reaction of $WCl_4(C_3H_7CN)_2$ with pyridine in butyronitrile. This reaction gave two products, one which was soluble in benzene and another which was insoluble in benzene. The soluble product will be called $WCl_4(C_5H_5N)_2$(II). The insoluble product will be called pyridine adduct(III).

The infrared spectra of the products obtained by both methods are given in Tables 8A to 10A. The bands of pyridine which are shifted by coordination are those at 601 and 403 cm^{-1}. The appearance of a band in the region 1235 to 1250 cm^{-1} is also characteristic of pyridine complexes (26). In $WCl_4(C_5H_5N)_2$(I) a band was present at 1240 cm^{-1}, the 601 cm^{-1} band was shifted to 625 cm^{-1} and the 403 cm^{-1} band to 449 cm^{-1}. Since no corresponding bands of free pyridine were present, the complex appears to contain only coordinated pyridine.

The far infrared spectrum of $WCl_4(C_5H_5N)_2$(I) is given in Table 8. This complex shows only one tungsten chloride stretching band which sharpens but does not split at low temperature. Even at low temperature the band is unsymmetrical and has a relatively wide line width (30 cm^{-1}). The situation is quite similar to that observed with $WCl_4(CH_3CH_2CH_2CN)_2$. As

Table 8. Far infrared spectrum of $WCl_4(C_5H_5N)_2$(I) (200-500 cm^{-1})

$(cm^{-1})^a$		$(cm^{-1})^b$
221 m,br	Unassigned	225 m,sh 233 w,br
320 vs,br	W-Cl stretch	320 vs,br
449 m,sh	Ligand band	448 m,sh

[a] Room temperature.

[b] Low temperature.

with that complex, the trans configuration is tentatively assigned, though there is some doubt about the assignment.

Study of the spectra of both products from the reaction of $WCl_4(CH_3CH_2CH_2CN)_2$ with pyridine indicates that this is not a simple substitution reaction leading to formation of pure $WCl_4(C_5H_5N)_2$.

The near infrared spectrum of $WCl_4(C_5H_5N)_2$(II) is simply characteristic of coordinated pyridine. The spectrum of pyridine adduct(III) however, also contains bands at 750, 1262, and 1531 cm^{-1}. These extraneous bands are probably indicative of impurities due to attack on the ligand during the course of the reaction. The far infrared spectra of the two products are more instructive. The number of weak broad bands in both spectra indicates that neither substance is a pure compound. The spectra in the metal-halogen stretching region are interesting in that $WCl_4(C_5H_5N)_2$(II) has a strong band at 336 cm^{-1}

and a shoulder at 296 cm^{-1}, while pyridine adduct(III) has a strong band at 299 cm^{-1} and a shoulder at 329 cm^{-1} (Figure 5). This also would seem to indicate that more than one product is present and that complete separation was not accomplished by extraction with benzene. Taking the sample to low temperature before recording the infrared spectrum seemed to enhance the weak bands present at room temperature, but did not help to define the structure of the product.

The X-ray powder patterns of both products, which gave analytical data corresponding to $WCl_4(C_5H_5N)_2$ were recorded. They are compared in Table 9 with the powder pattern of the product Brown prepared by reaction of WCl_4 with pyridine (10). The powder pattern of the complex prepared by reaction of the ethyl sulfide adduct with pyridine was identical, aside from a few intensity variations, with that obtained by Brown for $WCl_4(C_5H_5N)_2$. The powder pattern of the product from the reaction of the butyronitrile adduct with pyridine was very different. This is in agreement with infrared data and also suggests that this product was not a simple pyridine bis adduct.

The infrared spectrum of WCl_4(bipy), bipy = 2,2'-bipyridine, is given in Table 11A. Characteristics of coordinated bipyridine in the near infrared region are splitting of a band at 760 cm^{-1}, (out of plane deformation vibrations of two equivalent sets of four adjacent hydrogen atoms) and a rise in frequency of a band at 1590 cm^{-1} (C-N stretch) (27). In this

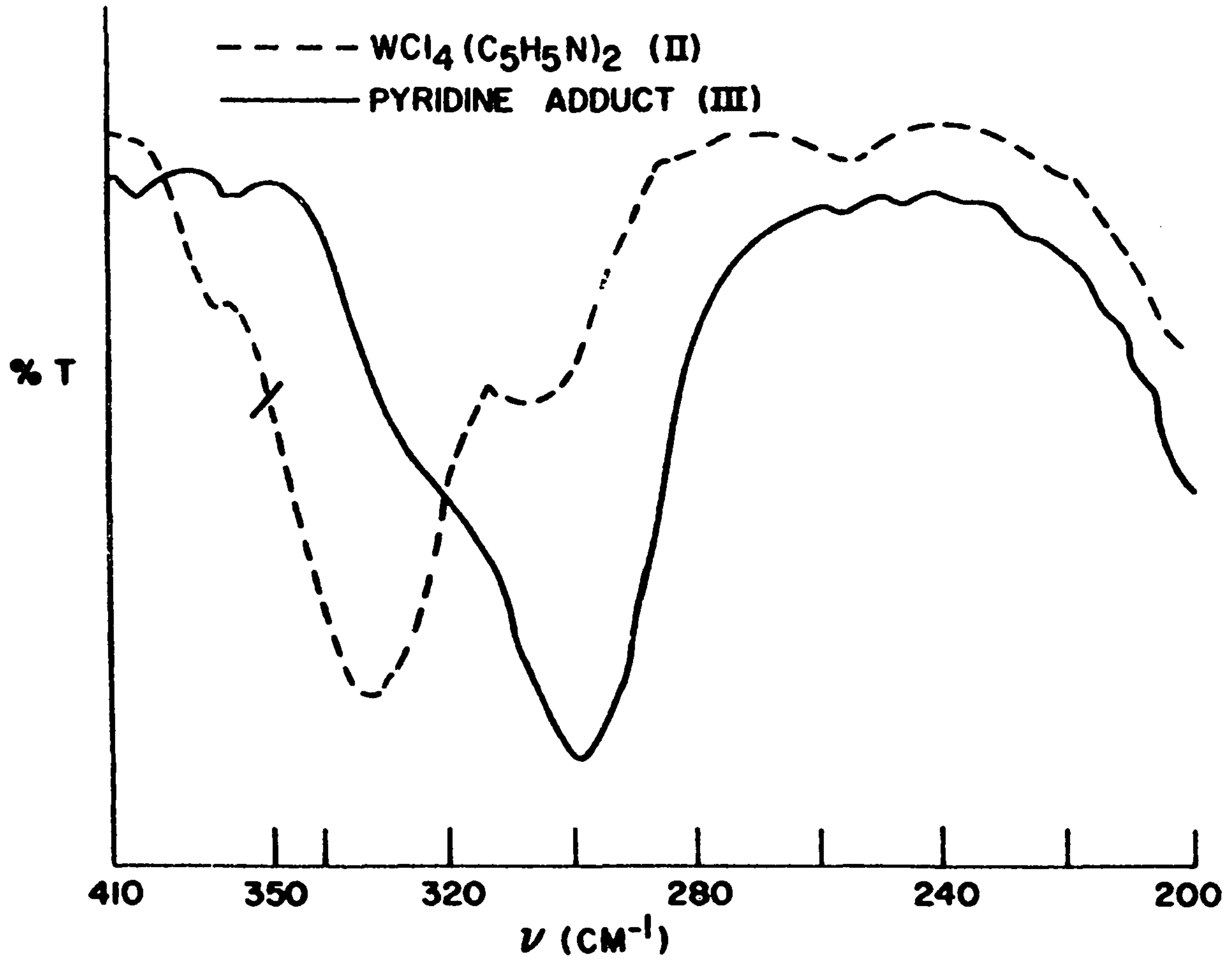

Figure 5. Far infrared spectrum of pyridine adducts

Table 9. X-ray diffraction d-spacings (Å) for $WCl_4(C_5H_5N)_2$

$WCl_4(C_5H_5N)_2$[a]	$WCl_4(C_5H_5N)_2(I)$[b]	$WCl_4(C_5H_5N)_2(II)$
6.43 vvs	6.50 vvs	9.34 s
6.10 vvs	6.18 s	8.68 s
5.14 vs	5.16 s	7.46 s
4.13 vs	4.13 w	6.98 w
4.13 w		6.67 vs
3.91 vw	3.97 w	6.43 vvs
3.82 vs	3.80 vs	6.09 vs
3.69 vw	3.71 w	5.48 w
3.64 vw	3.40 vvw	5.03 w
3.26 vvw	3.24 s	4.70 vw
3.20 vw	3.23 w	4.32 w
3.12 vs		3.83 s
2.79 vw	2.78 vs	3.63 w
2.67 vvw	2.67 vw	3.36 vw
2.55 s	2.56 s	3.02 s
2.49 w	2.49 w	2.82 w
2.42 vw	2.40 vw	2.55 s
2.33 s	2.34 s	2.47 w
2.29 vw	2.28 s	2.23 s
2.15 vvw	2.13 w	1.98 vvw
2.11 vvw	2.09 vw	1.86 vvw
2.09 vvw		

[a] Product from reaction of WCl_4 with pyridine.

[b] Product from reaction of $WCl_4[(C_2H_5)_2S]_2$ with pyridine.

complex the 760 cm^{-1} band was split into two bands at 724 and 769 cm^{-1} and the 1590 band shifted to 1597 cm^{-1}. No uncoordinated bipyridine was present.

The far infrared spectrum in the region 200-500 cm^{-1} is recorded in Table 10.

Going to low temperature caused very little change in the far infrared spectrum. The presence of multiple tungsten-

Table 10. Far infrared spectrum of WCl_4(bipy) (200-500 cm^{-1})

$(cm^{-1})^a$		$(cm^{-1})^b$
245 w,br	Unassigned	250 w,br
307 s,br		308 s,br
323 s,br		322 s,br
331 s,br	W-Cl stretch	
346 s,br		340 s,br
423 m,sh	Ligand ring torsion	426 m,sh

[a] Room temperature.

[b] Low temperature.

chloride stretching frequencies and the constrained nature of the bidentate ligand are consistent with a cis configuration of the nitrogen atoms in a monomeric adduct. However, as discussed subsequently, the magnetic susceptibility data for the compound suggests that the structure is more complicated.

Nuclear Magnetic Resonance Studies

The criterion for observation of nmr signals in paramagnetic complexes is that the electron spin relaxation rate in a complex $1/\tau e$ must be greater than the nuclear electron hyperfine interaction, i.e. $|a\tau_e| << 1$ where a is the nuclear electron isotropic hyperfine interaction constant (28). Sharp signals have been observed for several ions which are either isoelectronic with or have an electron configuration which is similar to paramagnetic tungsten(IV) complexes. These include nickel(II) and vanadium(III). As a result it was felt that an investigation of the nmr of several of the more soluble tungsten(IV) complexes might be profitable.

The only complexes with sufficient solubility in appropriate solvents were $WCl_4[(C_2H_5)_2S]_2$, $WCl_4(CH_3CH_2CH_2CN)_2$ and $WBr_4(CH_3CH_2CH_2CN)_2$. The spectra of the butyronitrile complexes were recorded in deuterated benzene on the Varian HA-100 spectrometer. A small amount of benzene impurity in the solvent served as an internal standard since tetramethylsilane obscured a sample signal. The signals observed are recorded in Table 11. The shift Δv was defined as the difference between the shift of a proton in the paramagnetic complex measured in a specific solvent and the shift of the same proton in the uncomplexed ligand measured in the same solvent. The signals were sharp for the methyl group but broadened for the methylene. The failure to observe a signal for the methylene group bound to the nitrile C ≡ N functionality was due to either severe broadening of the signal or a shift too far upfield to be observed by the instrument. Solubility limitations were no doubt a factor; the signals were very weak because of this problem.

Table 11. NMR spectra of $WX_4(CH_3CH_2CH_2CN)_2$ (X = Cl, Br) complex

		Δv(cps)	
	CH_3-	-CH_2-	-CH_2-CN
$WCl_4(CH_3CH_2CH_2CN)_2$	+112	+591	not observed
$WBr_4(CH_3CH_2CH_2CN)_2$	+71	+543	not observed

The spectrum of $WCl_4[(C_2H_5)_2S]_2$ was observed from -40° to 20° in dichloromethane and from 34° to 70° in deuterated benzene. The shifts observed are recorded in Table 12.

Table 12. NMR spectrum of $WCl_4[(C_2H_5)_2S]_2$

Temperature °C	$\Delta v(cps)^a$	
	CH_3-	-CH_2-
-40	-431	not observed
-20	-433	not observed
0	-431	not observed
20	-433	+1431
	$\Delta v(cps)^b$	
	CH_3	-CH_2-
34	-397	1100
40	-397	1142
50	-395	1182
60	-391	1242
70	-393	1278

[a] Spectrum in CH_2Cl_2.

[b] Spectrum in d^6-benzene.

The solvent effect was quite pronounced. This indicates that it would be preferable to reference the shift against that of a similar diamagnetic complex rather than uncomplexed ligand. Unfortunately such data were not readily available for the complexes being studied.

The shifts in the ethyl sulfide complex are alternating in sign in contrast to the butyronitrile complex in which all observed shifts were upfield. The shifts showed an interesting temperature dependence, with the signals of the methylene protons shifting upfield with rising temperature. However, over the temperature range observed the signal of the methyl protons is virtually temperature independent. The sharpness of the signals also shows a marked temperature dependence. Though this effect was also observable in the signal of the methyl protons it was more pronounced in the signal of the methylene protons. The signal collapsed completely below 20° so it was unobservable at 0°. The dependence of line width upon temperature for the methyl and methylene protons is illustrated in Figure 6.

A number of attempts have been made to quantitatively analyze paramagnetic shifts (29,30). The first problem is to separate the contribution of the contact shift (shift resulting from the presence of unpaired electron density at the resonating nucleus) and the dipolar or pseudocontact shift (shift resulting from a dipolar interaction between the electronic magnetic moment and the nuclear spin). This in itself is a difficult problem requiring single crystal magnetic anisotropy data. Another more approximate method is to compare the shifts of a magnetically anisotropic complex with those of a very similar isotropic complex and assume the difference in the paramagnetic shifts is the dipolar contribution. This has been done for a number of cobalt and nickel complexes (31).

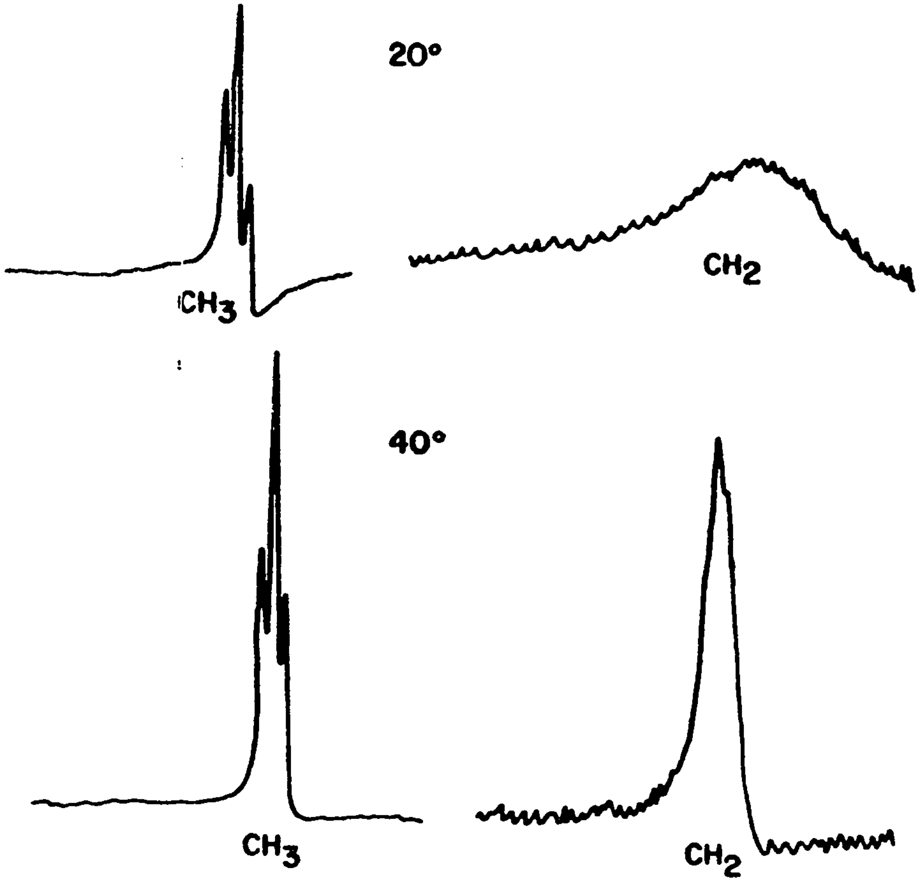

Figure 6. Intensity of nmr signals as a function of temperature

Unfortunately the necessary data are not available for application of either method to tungsten(IV) complexes.

Kurland and McGarvey (32) have pointed out that the assumption made in derivation of the basic equations which are often used to define contact and dipolar shifts are the following: (1) there are no thermally populated excited state energy levels in the absence of a magnetic field; (2) there is no zero field splitting; (3) there are no more than first order effects in the magnetic moment from spin-orbit coupling. When these effects are considered the equations rapidly become very complicated. Since these basic assumptions do not hold for tungsten(IV) more study is needed before a quantitative approach to the data can be attempted.

Magnetic Susceptibility

Measurements of magnetic susceptibility over the temperature range 20° to 297°K were made for a series of six tungsten (IV) chloride complexes, WCl_4L_2. Compounds of the following ligands were studied: ethyl sulfide, tetrahydrothiophene, butyronitrile, triphenylphosphine, pyridine, and bipyridine. Synthetic methods utilized in preparing the complexes and analytical data for the compounds on which susceptibility measurements were made are given in the Experimental section.

The data obtained was processed using the method of Honda and Owen for determination of field dependence of the magnetic susceptibility. A least squares fit of the apparent susceptibility and field strength to the equation

$$\frac{\Delta fi}{\Delta Fi} = m\ \chi g + C\sigma\ \frac{1}{\Delta Hi}$$

where: f = force acting on the substance in dynes,

m = mass of substance in grams,

χg = gram susceptibility, emu/gram,

H = magnetic field, oersted

C = concentration of ferromagnetic impurity

σ = saturation magnetization of the impurity dyne-cm/oersted

was used. The intercept gave values of χg which were corrected for ferromagnetic impurity. A detailed description of the computer program used to process the data was given by Converse (13). The program included a correction for the diamagnetism of the Teflon sample container. The value used for the gram susceptibility of Teflon was that determined by Converse, (-0.350×10^{-6} emu/gram). A determination of the temperature dependence of the gram susceptibility of Teflon was made down to 33°K. The susceptibility was found to be virtually temperature independent (Table 12A), with the average value -0.3637×10^{-6} emu/g. The variation of this value from that found by Converse could be due to a variation in the composition of the Teflon in the bucket used or variation in the force constants of the magnet. Since several different buckets were used and since the magnet force constants used were those determined by Converse, his value for the gram susceptibility of Teflon was used for all corrections. An error in this correction would have a slight effect on the absolute values of the susceptibilities measured, but no effect on the temperature dependence of the data.

The magnetic susceptibilities of the complexes are given in Tables 13A-19A of the Appendix. For the seven complexes examined the temperature dependence of the data was quite similar for all but $WCl_4(C_5H_5N)_2$(II), and the bipyridine complex, WCl_4(bipy). These will be discussed separately.

The data were corrected for the diamagnetism of the atomic core electrons. The corrections used were calculated from additive atomic constants listed by Selwood (33). The corrected values are listed as $\chi_M - \chi_D$ (molar susceptibility-diamagnetic correction). The variation of the susceptibility data with temperature for the complexes WCl_4L_2 (L = C_5H_5N, $(C_6H_5)_3P$, C_3H_7CN, $(C_2H_5)_2S$, C_4H_8S) followed the following pattern. The values of molar susceptibility rose steadily as the temperature was lowered to approximately 100°K. The values then leveled off and became virtually temperature independent until about 40°K at which point the values again began to slowly increase. The magnitude of this rise in susceptibility below 40°K varied from a negligible amount in the butyronitrile complex to a maximum amount in the ethyl sulfide and triphenylphosphine complexes. This variation is shown in Figure 7. A plot of $\chi_M-\chi_D$ versus 1/T over the range 20° to 60°K for these complexes revealed that the data exhibits Curie law behavior over the range. This is illustrated for $WCl_4[(C_6H_5)_3P]$ and $WCl_4(C_5H_5N)_2$ in Figures 8 and 9. A least squares fit of the data to the Curie equation, $\chi_M = NB^2\mu^2/3kT$ gave the values listed in Table 13 for the apparent moment over this temperature range.

Table 13. Apparent magnetic moments of WX_4L_2 complexes (20-60°K)

Complex	Apparent moment, B.M.
$WCl_4(CH_3CH_2CH_2CN)_2$	negligible
$WCl_4(C_4H_8S)_2$	0.18
$WCl_4(C_5H_5N)_2$	0.21
$WCl_4[(C_6H_5)_3P]_2$	0.23
$WCl_4[(C_2H_5)_2S]$	0.25

Because the susceptibility conformed to the Curie law and the apparent moments were so low, it was felt that this effect was due to a small amount of paramagnetic impurity present in variable amounts in the complexes. The impurity only became apparent at very low temperature as 1/T became large. On this assumption a correction to the molar susceptibility for para-

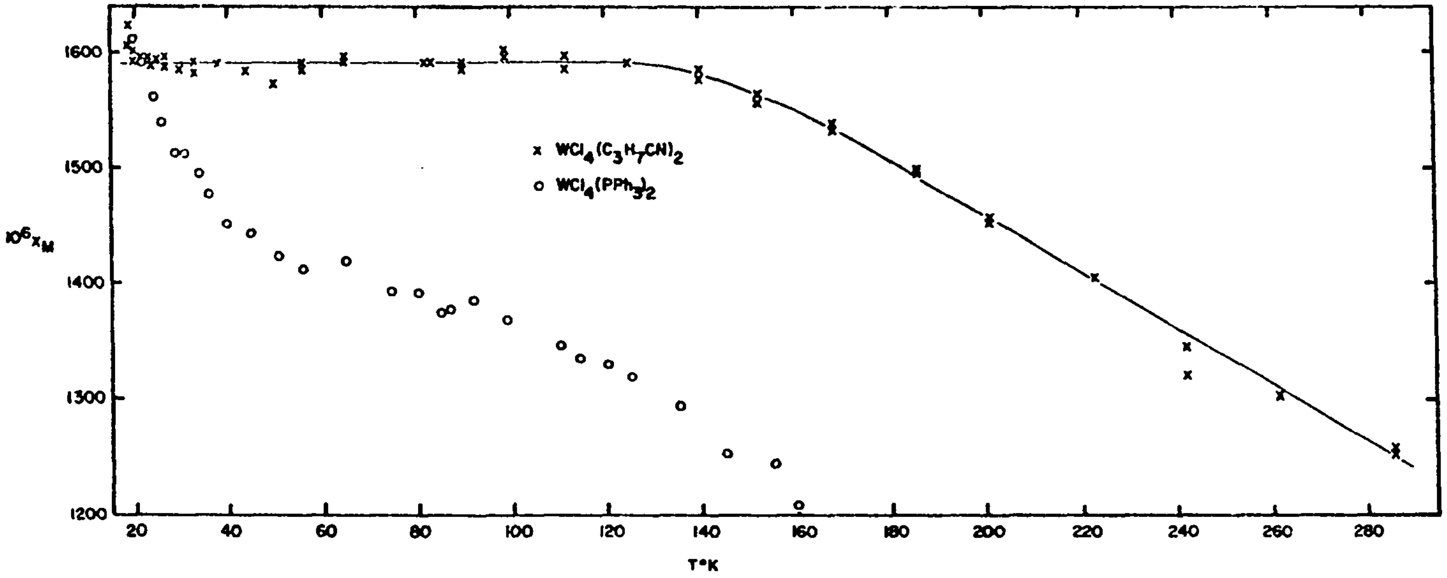

Figure 7. Magnetic susceptibilities of $WCl_4(C_3H_7CN)_2$ and $WCl_4[(C_6H_5)_3P]_2$

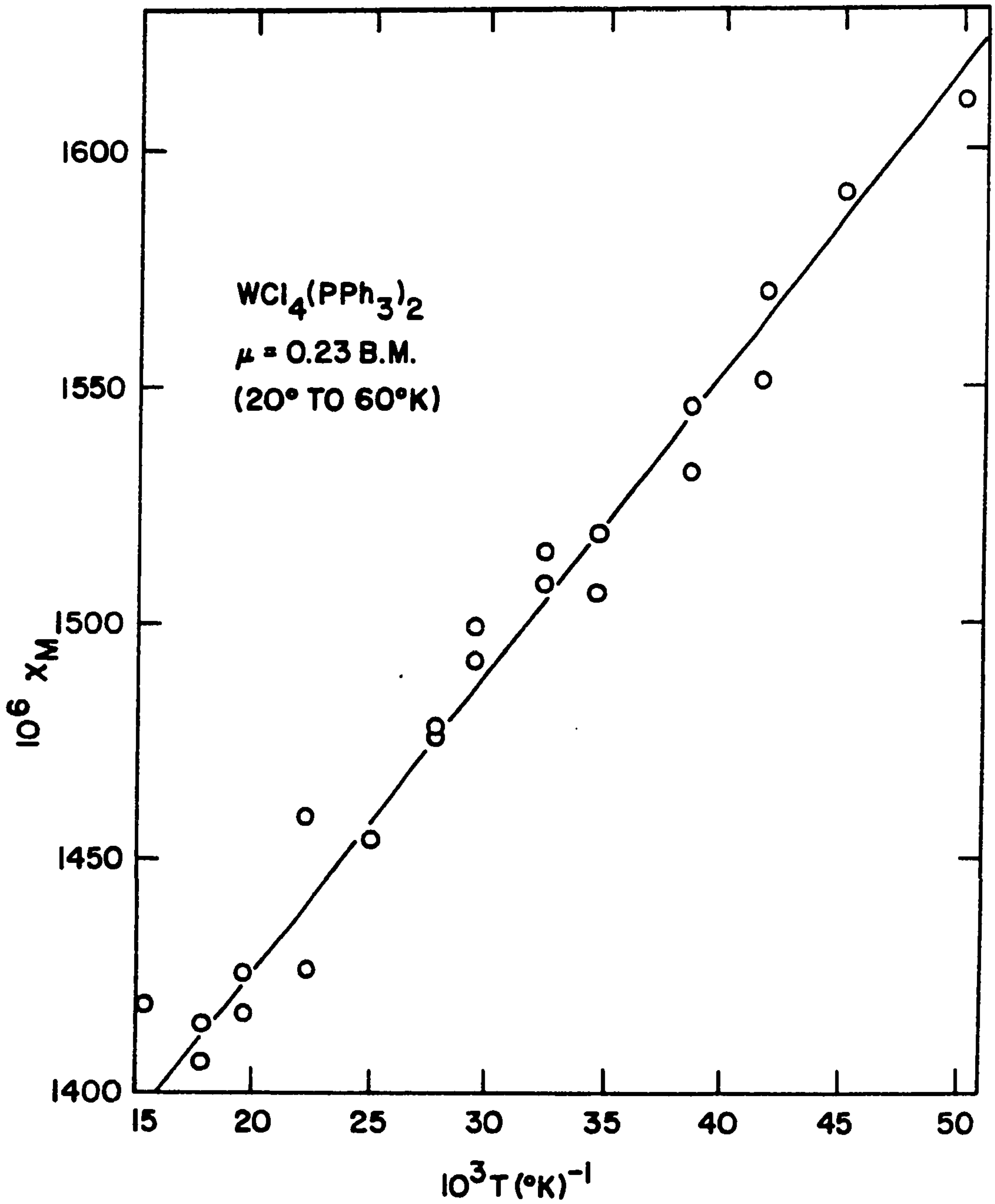

Figure 8. Low temperature magnetic susceptibility of $WCl_4[(C_6H_5)_3P]_3$

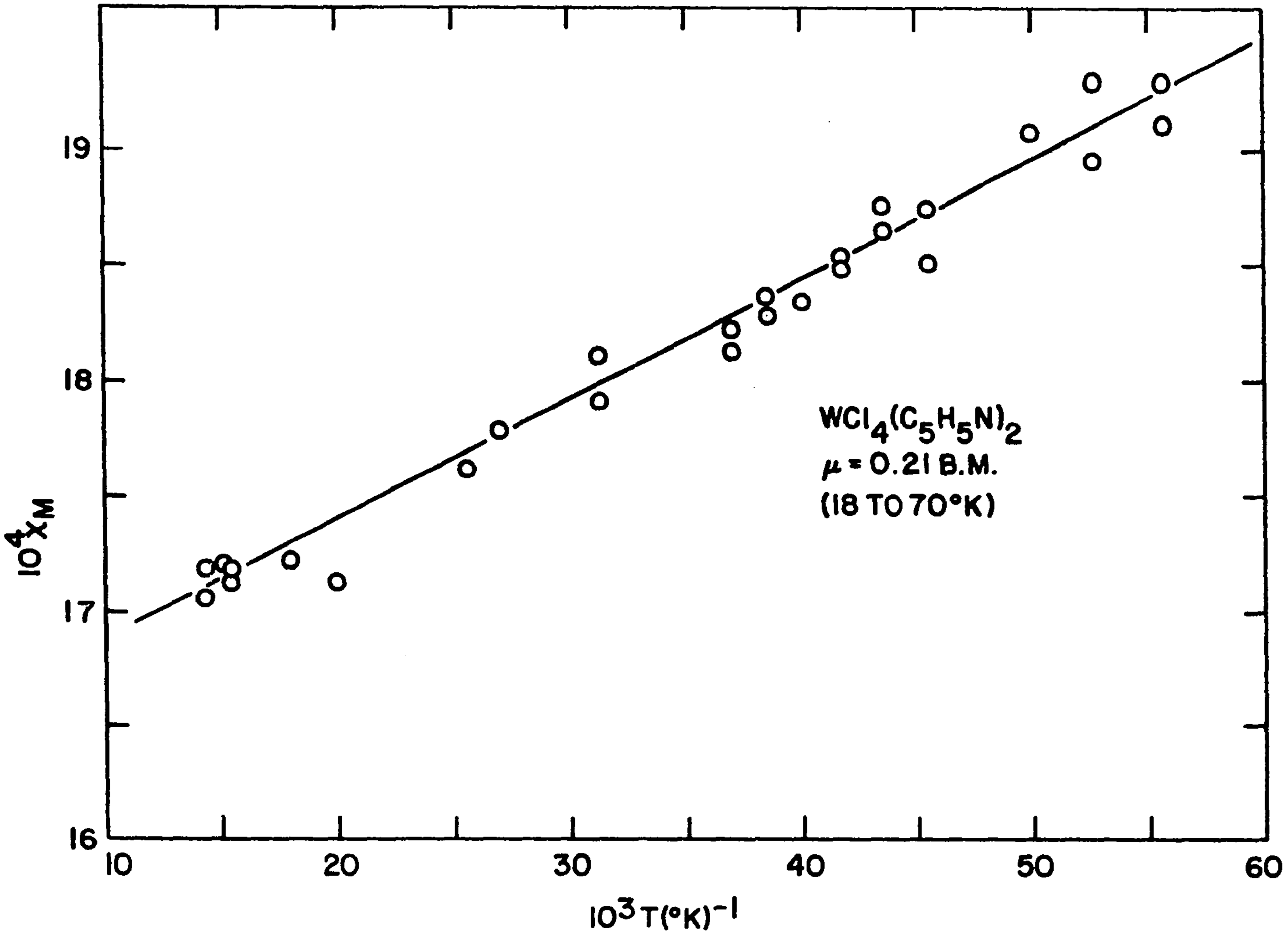

Figure 9. Low temperature magnetic susceptibility of $WCl_4(C_5H_5N)_2$

magnetic impurities χ_{imp} was applied over the entire temperature range. This correction was calculated from the previously determined apparent moment at low temperature via the equation $\chi_{imp} = NB^2\mu^2_{app}/3kT$. The χ_{corr} in Tables 13A to 19A is the observed molar susceptibility corrected for diamagnetism of the core and for paramagnetic impurity, $\chi_{corr} = \chi_M - \chi_D - \chi_{imp}$.

The esr spectra of several of the complexes were studied to better determine the nature of the paramagnetic impurities. The butyronitrile complex showed a signal at g = 1.77 that was barely detectable even at the highest sensitivity setting of the instrument. The pyridine complex gave a weak signal at g = 1.75. The spectrum of the ethyl sulfide complex was taken at low temperature in a toluene glass. In this medium the complex showed an anisotropic signal with $g_1 = 1.80$, $g_2 = 1.84$, and $g_3 = 1.87$. The relative intensities of the signals agree with the magnitude of the "apparent moments" calculated from the susceptibility data, with the butyronitrile complex showing the least impurity and the ethyl sulfide the most. The g-factors indicate that the impurities are odd-electron tungsten species, but it is not possible to differentiate between tungsten(III) and tungsten(V) species without further study. Reported g-factors of tungsten(V) have been near 1.75 (34). No g-factors have been reported for tungsten(III), however, an approximate calculation of the expected g-factor can be made. For a d^3 system the ground state term is $^4A_{2g}$ so the expression for the g-factor is $g = 2(1-4\lambda/10Dq)$. Approximate values of λ and 10Dq for tungsten(III) are 600 cm^{-1} and 20,000 cm^{-1} (35). Substituting these values into the above equation gives g = 1.76. Since the values expected are approximately the same for both tungsten(III) and tungsten(V), it is not possible to differentiate between the two by observation of the g-factor. Tungsten(III) would likely be present as WCl_3L_3 complexes, and tungsten(V) as oxyhalide complexes. A calculation of the weight fraction of each type of impurity needed to give an "apparent moment" of 0.2 B.M. was made by assuming that over the temperature range considered the impurity obeyed the Curie law, and that μ of the tungsten(IV) complex was zero. Assuming tungsten(III) has 3 unpaired electrons the weight fraction needed was 0.00266, while a weight fraction of 0.0133 of tungsten(V) was needed. No tungsten-oxygen stretching band was discerned in the infrared spectra of the complexes. However it is questionable if oxyhalide impurity present in such small weight fraction would give rise to a detectable band in the infrared. When the synthetic methods used to prepare the various complexes are considered, it appears that the conditions which favor elimination of impurity are a deficiency of the reacting ligand, moderate reaction temperatures, and a noncomplexing solvent which can be used to wash or recrystallize the final product.

Comparison of the observed values of χ_M for the pyridine adduct, $WCl_4(C_5H_5N)_2$, synthesized by reaction between pyridine and $WCl_4[(C_2H_5)_2S]_2$ in benzene, with those observed by Brown on the complex obtained by direct reaction of pyridine with WCl_4 and those observed by Converse for the complex obtained by reduction of WCl_5 with pyridine is made in Figure 10. Even though the complexes were synthesized by very different methods the agreement of the data is good. This agreement is in accord with infrared and X-ray powder pattern data which also indicate that these methods give the same product.

In contrast the values found for χ_M of $WCl_4(C_5H_5N)_2$(II) differ greatly, even though analytical data indicate the stoichiometry is the same as $WCl_4(C_5H_5N)_2$(I). Very low values of χ_M were found from 86° to 297°K (Table 18A). A plot of the corrected susceptibility versus 1/T was linear. From the slope of the line, as found from a linear least squares treatment of the data, the value 0.63 B.M. was calculated for μ_{eff}. The esr spectrum of this product gave a relatively strong signal with g = 1.77. For pure tungsten(IV) complexes an esr signal should not be observed because the electronic levels do not exhibit Kramers degeneracy. Thus it appears that a component present as either tungsten(III) or tungsten(V) species gives rise to the observed signals. The low magnetic moment suggests that the product may be a mixture of diamagnetic and paramagnetic components. Further studies are needed to completely separate and identify the products of this reaction.

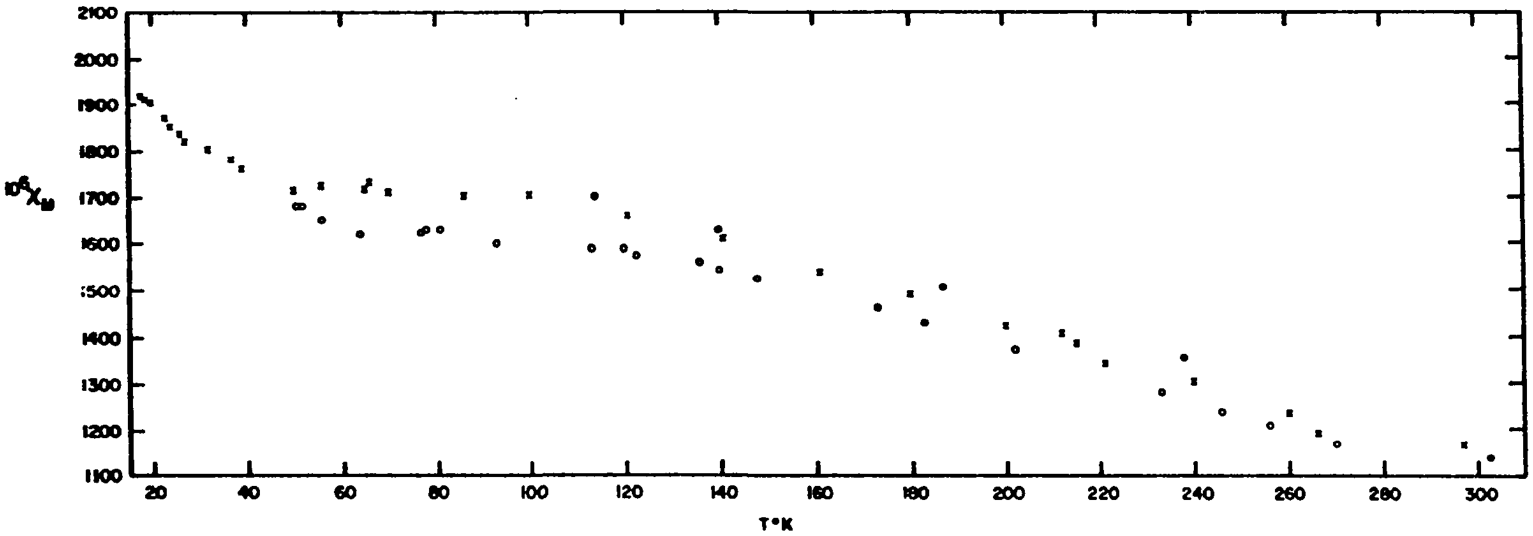

Figure 10. Magnetic susceptibility of $WCl_4(C_5H_5N)_2$ (o, Converse (13); •, Brown (11); x, this work)

The susceptibility of WCl_4(bipy) is given in Table 19A along with values of μ_{eff}. A plot of χ_M versus 1/T for the complex was not linear. However, when the data were plotted according to the Curie-Weiss law, $1/\chi_M-\chi_D$ versus T the plot was linear down to 60°K, but showed a slight curvature from 60° to 20°K. The intercept of the plot from 60° to 300°K gave a Weiss constant (θ) of -38°K, and the slope a value for μ_{eff} of 1.39 B.M. The room temperature magnetic moment 1.62 B.M. agreed with the value reported by Hull and Stiddard for the same complex prepared by oxidation of $W(CO)_4$bipy with chlorine (17). It is not known whether the deviation from Curie law behavior in this complex is caused by exchange interactions or thermal population of higher energy levels. The reason that the temperature dependence of this complex was different from the other tungsten(IV) complexes is not known. It is possible that the complex is not a simple cis monoadduct but instead has a more complex structure, for example a polymer or complex salt of the type $[W(bipy)_2Cl_2]^{2+}WCl_6{}^{2-}$. Complete characterization of the complex was made difficult by its lack of solubility.

Theoretical

The ground state free ion term for a d^2 electron configuration is ^3F. The action of a cubic ligand field and electron repulsion on this term leads to a $^3T_{1g}$ term being lowest in energy. The splitting of this $^3T_{1g}$ term due to spin-orbit coupling and low symmetry in a complex has been discussed by several authors (36,37). Ballhausen has calculated the energy levels obtained by applying spin-orbit coupling as a perturbation to the ${}^3T_{1g}$ term. When one considers the effect of a D_{4h} or C_{2v} low symmetry field on these energy levels they split as shown in Figure 11. No attempt is made to assign ordering of the levels. It can be seen that the effect is to remove all or nearly all of the degeneracy of the levels. In the C_{2v} case all levels would be nondegenerate and hence would suffer no first order Zeeman interaction with the applied magnetic field.

Magnetic susceptibility can be expressed in the following way:

$$\chi_i = \frac{N \sum\limits_{nm} \left(\frac{[E^{(1)}_{nm}]^2}{kT} - 2E^{(2)}_{nm} \right) e^{-E^0_n/kT}}{\sum\limits_{n} e^{-E^0_n/kT}}$$

where n and m are quantum numbers n designating an energy level and m the degeneracy of that level with no applied field,

and, $E^{(1)}_{om} = (\Psi_{om}|\mu_i|\Psi_{om})$,

$$E^{(2)}_{om} = \sum_{nm} \frac{|\Psi_{om}|\mu_i|\Psi_{nm}|^2}{E_o - E_n}$$

$$\mu_i = \beta(L_i + 2S_i).$$

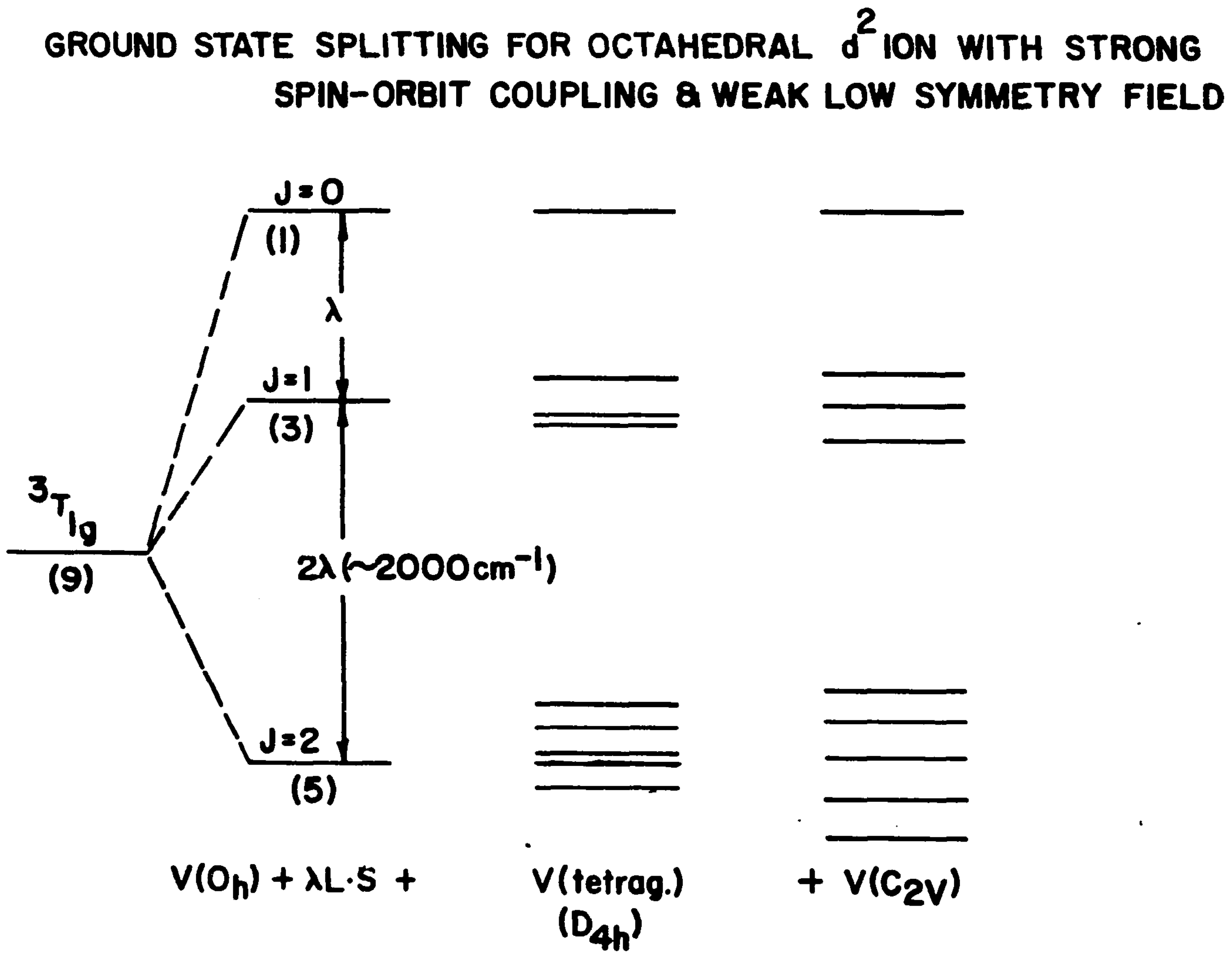

Figure 11. Energy level diagram for d^2

When the ground state is nondegenerate and magnetically inactive, contribution of the term $|E_{nm}^{(1)}|^2/kT$ is zero and,

$$\chi_i = \frac{N \sum\limits_{nm} (-2E_{nm}^{(2)})\, e^{-E_n^\circ/kT}}{\Sigma e^{-E_n^\circ/kT}} \tag{2}$$

Assuming that only the next highest level is thermally populated over the temperature range considered,

$$\chi = \frac{N\beta^2(2E_{00}^{(2)} + 2E_{0\pm1}^{(2)}\, e^{-\delta/kT})}{1 + e^{-\delta/kT}} \tag{3}$$

where δ is the energy separation between the two lowest levels.

Equation 3 can also be expressed as the sum of susceptibilities,

$$\chi = \frac{\chi_o + \chi_1\, e^{-\delta/kT}}{1 + e^{-\delta/kT}}$$

To obtain estimates of the parameters in this equation, we make the following approximations. If we let $y = e^{-\delta/kT}$ then

$$\chi = \frac{\chi_o + \chi_1(y)}{1 + y}$$

Expansion of $1/1+y = 1 - y + y^2 - y^3 + \cdots$, so

$$\chi = (\chi_o + \chi_1 y)(1 - y + y^2 - y^3 + \cdots)$$

$$= \chi_o + \chi_1 y - \chi_o y - \chi_1 y^2 + \chi_o y^2 + \chi_1 y^3 - \chi_o y^3 \cdots$$

$$= \chi_o - (\chi_o - \chi_1)y + (\chi_o - \chi_1)y^2 - (\chi_o - \chi_1)y^3 + \cdots$$

Using successive approximation, we assume only the first term contributes significantly, over the temperature interval covering onset of population of the first excited level. So, $\chi_{corr} = \chi_o - (\chi_o - \chi_1)\, e^{-\delta/kT}$.

When log $(\chi_o - \chi_{corr})$ is plotted versus 1/T the slope is equal to $-\delta/k$ (2.303) and the intercept to log $(\chi_o - \chi_1)$.

The term χ_o is the constant value that χ_{corr} attains at low temperature. Thus the value of χ_o is easily obtained directly from the experimental data.

Log $(\chi_o - \chi_{corr})$ versus 1/T was plotted from the temperature where χ_{corr} first deviated significantly from χ_o (usually 100° to 140°K) up to 200°K. A sample plot, that of $WCl_4(C_3H_7CN)_2$, is shown in Figure 12.

The values of δ and χ_1 obtained by a linear least squares fit of the data are given in Table 14 along with values of χ_o. These values were then substituted into the original expression,

$$\chi_{corr} = \frac{\chi_o + \chi_1 e^{-\delta/kT}}{1 + e^{-\delta/kT}}$$

to give calculated values of χ.

In the cases where there was a large standard deviation in the values of χ_1 and δ, the values of the parameters which

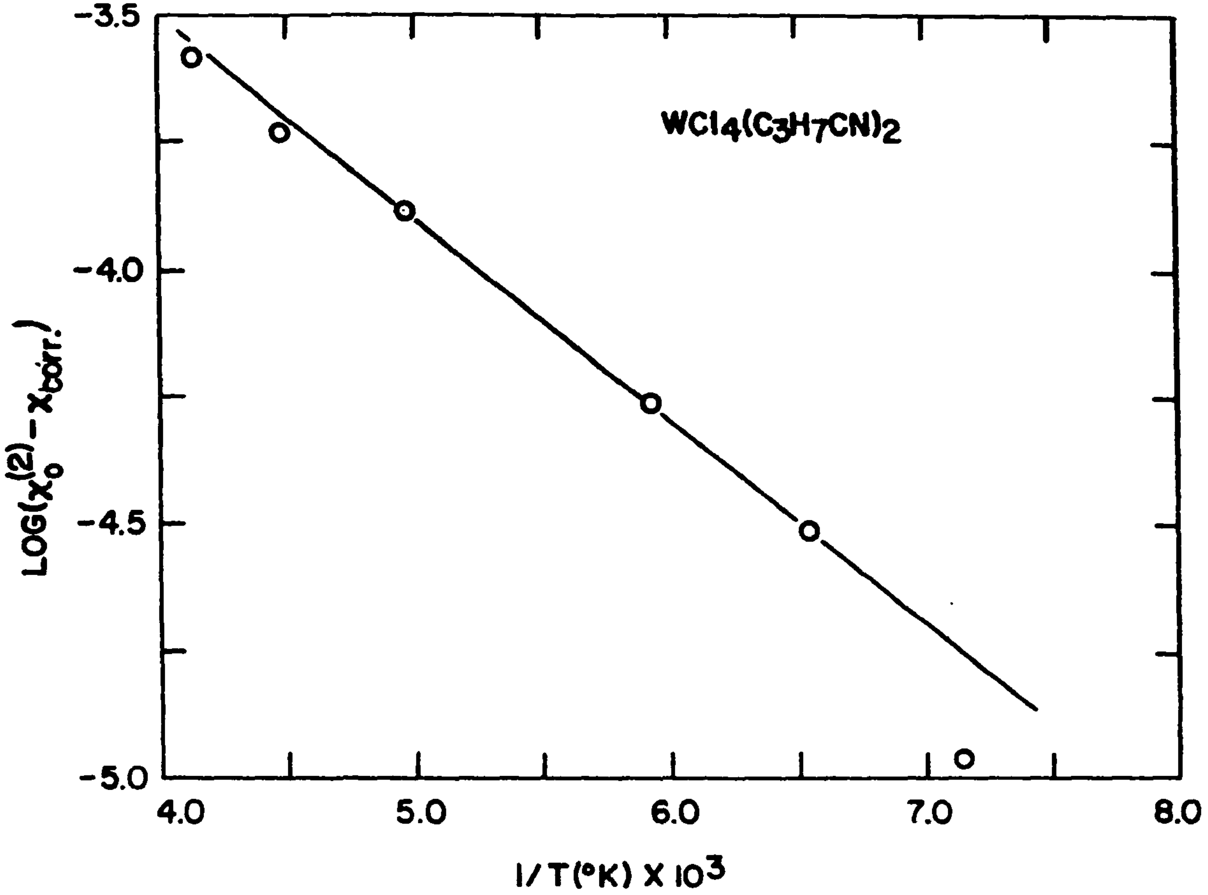

Figure 12. Plot used for calculation of δ and χ_1

Table 14. Values of χ_0, χ_1 and δ_1

Complex	$\chi_0(10^{-6})$ emu/mole	$\chi_1(10^{-3})$ emu/mole	δ/cm^{-1}
$WCl_4(C_5H_5N)_2$	1848	-6.277 ± 2.7	509 ± 47
$WCl_4(CH_3CH_2CH_2CN)_2$	1817	-7.958 ± 1.2	608 ± 17
$WCl_4[(C_6H_5)_3P]_2$	1754	-8.679 ± 3.0	506 ± 35
$WCl_4(C_4H_8S)_2$	2065	-1.953 ± 0.4	348 ± 12
$WCl_4[(C_2H_5)_2S]_2$	1926	-20.40 ± 12.3	642 ± 100

gave the best agreement between calculated and experimental susceptibility were found by trial and error. Comparison of calculated and experimental values of χ_{corr} for the complex are given in Tables 20A to 24A along with the values of the parameters which were used to calculate the susceptibility. The best fit was found for data from the butyronitrile and tetrahydrothiophene complexes. The largest standard deviation in the values of χ_1 and δ was for the ethyl sulfide complex. Deviation of the calculated from experimental values was greatest at room temperature in all cases. This may indicate that the simplifying assumptions made in deriving the equations are not valid at these temperatures. The model does, however, appear to be quite successful in approximating the experimental data over most of the temperature range studied.

Since the infrared spectra indicated that data for both _cis_ and _trans_ complexes were obtained and since the temperature dependence of the susceptibility varied little from complex to complex, it appeared that the magnetic properties of tungsten (IV) were very similar for both configurations. Agreement of calculated with experimental data was dependent on the quality of the experimental data and purity of the complex. It is difficult to determine if the poor agreement for the ethyl sulfide complex was due to the fact that its stereochemistry is different from the other complexes or the fact that it contained a larger amount of impurities.

The model discussed applies to the situation where all degeneracy of the levels has been removed. The possibility that the level above the ground state is magnetically active (subject to first order Zeeman splitting) must also be considered. This is the situation that might be expected for a _trans_ (D_{4h}) complex, as shown in Figure 11. It is possible that the data can be fitted to an equation of the form,

$$\chi = \frac{\chi_o + \left(\frac{a}{T} + b \right) e^{-\delta/kT}}{1 + 2e^{-\delta/kT}}$$

It is not possible however to estimate a and b by simple graphic methods. Any further data which would help to distinguish between these two possibilities such as low temperature heat capacity data would be fruitful in contributing to the solution of this problem.

SUMMARY

Tungsten(IV) chloride and tungsten(V) chloride were prepared by reduction of higher halides with tungsten hexacarbonyl. In the case of WCl_4 the product was more reactive toward organic ligands than products obtained *via* other methods.

Using this tetrahalide and the complexes which could be prepared from it a series of analytically pure tungsten(IV) chloride complexes WCl_4L_2 were synthesized. The ligands used were nitriles, sulfides, triphenylphosphine, and pyridine. These complexes were structurally characterized by examination of their infrared spectra, in particular the study of the metal-halogen stretching frequencies. Infrared spectra were recorded at low temperature to get better resolution of these bands, which tend to be quite broad at room temperature.

Magnetic susceptibilities of a series of complexes, WCl_4L_2, were measured down to 20°K using a magnetic balance equipped with a liquid helium cryostat. The magnetic susceptibility exhibited very similar temperature dependence for five of these compounds: $WCl_4(C_5H_5N)_2$, $WCl_4[(C_6H_5)_3P]_2$, $WCl_4(C_3H_7CN)_2$, $WCl_4(C_4H_8S)_2$ and $WCl_4[(C_2H_5)_2S]_2$. A model for calculation of the susceptibilities of these complexes was prepared which proved quite successful in reproducing the experimental data over most of the temperature range.

The susceptibilities of WCl_4(bipy) and a pyridine adduct

prepared by an alternate method behaved much differently. The temperature dependence of the bipyridine adduct indicated that it was probably not structurally similar to the other complexes. The pyridine complex prepared from $WCl_4(C_3H_7CN)_2$ and pyridine in butyronitrile, as evidenced by the unique temperature dependence of its susceptibility, appeared to have a more complicated structure than that of a simple adduct $WCl_4(C_5H_5N)_2$. Other evidence about the nature of the products from this reaction was obtained from infrared spectra.

A study of paramagnetic proton nmr shifts in the ethyl sulfide and butyronitrile adducts of tungsten(IV) halides was made. The temperature dependence of the line widths and shifts was studied for the ethyl sulfide complex. However a quantitative treatment of the data was not possible because of inadequate understanding of the several terms which may contribute to the shift in such complicated systems.

SUGGESTIONS FOR FUTURE WORK

The structure and properties of the tungsten halides prepared by reduction of the higher halides with tungsten hexacarbonyl were not thoroughly investigated and need further work. Very little characterization of the tungsten(V) chloride prepared by this method has been done. Studies to determine if it is identical with the product formed by other methods would be of value.

The stereochemistry of the complexes WX_4L_2 (X = Cl, Br; L = N, S or P donor ligand) could be more firmly established if Raman studies were done. Since complete infrared studies have been made it would be possible to check for coincident lines in the Raman spectrum, a situation expected for *cis* complexes but not for *trans*. Structural data on one or more of the complexes would also help in this respect. The butyronitrile, ethyl sulfide and tetrahydrothiophene complexes are crystalline and offer possibilities for a structure determination.

The study of paramagnetic shifts for tungsten(IV) offers many possibilities. Only a small amount of data has been recorded and it reveals several interesting features which merit further study. The theory of paramagnetic shifts particularly for systems such as tungsten(IV) needs development so the data can be better understood and utilized.

The difficulties encountered in preparing pure tungsten

(IV) complexes suggests that under the proper conditions tungsten(III) complexes could be prepared. Since very little work has been done on monomeric tungsten(III) complexes this would certainly be a worthwhile area to pursue.

More work is also needed to fully explain the magnetic properties of tungsten(IV). The model presented may be only one of several ways to successfully reproduce the experimental data. More discussion and attempts in this area are needed.

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APPENDIX

Table 1A. Infrared spectrum of $WCl_4(CH_3CN)_2$

Near infrared, $\nu(\mathrm{cm}^{-1})$[a]	Far infrared, $\nu(\mathrm{cm}^{-1})$[b]	Far infrared, $\nu(\mathrm{cm}^{-1})$[c]
945 m,vsh[d]	98 m,br	237 m,sh
1017 s,sh	110 w,br	245 w,br
1358 s,vsh	134 s,vbr	289 m,sh
2285 s,sh	148 s,sbr	320 s,br
2314 m,sh	235 m,sh	337 s,br
2319 m,sh	242 w,br	425 m,sh
	284 m,sh	435 m,sh
	325 vs,vbr	
	418 s,vsh	
	428 s,vsh	

[a] Room temperature.

[b] Room temperature.

[c] Low temperature.

[d] s = strong, m - medium, w = weak, v = very, sh = sharp, br = broad. (These abbreviations will be used in all subsequent tables).

Table 2A. Infrared spectrum of $WBr_4(CH_3CN)_2$

Near infrared, $\nu(\mathrm{cm}^{-1})$[a]	Far infrared, $\nu(\mathrm{cm}^{-1})$[b]	Far infrared, $\nu(\mathrm{cm}^{-1})$[c]
943 vw,sh	102 w,br	218 vs,sh
1020 m,sh	122 w,br	242 vs,sh
1354 s,vsh	130 w,br	250 vs,sh
2274 s,vsh	216 vs,br	287 w,br
2304 m,sh	245 vs,vbr	426 m,sh
2314 m,sh	283 m,sh	436 m,sh
	425 m,vsh	
	435 m,vsh	

[a] Room temperature.

[b] Room temperature.

[c] Low temperature.

Table 3A. Infrared spectrum $WCl_4(CH_3CH_2CN)_2$

Near infrared, $\nu(cm^{-1})$[a]	Far infrared, $\nu(cm^{-1})$[b]	Far infrared, $\nu(cm^{-1})$[c]
780 s,vsh	133 s,vbr	268 w,br
856 w,sh	150 m,br	327 s,br
1000 w,sh	265 w,br	345 s,br
1066 s,vsh	330 vs,vbr	428 w,sh
1004 w,sh	426 w,sh	
1257 m,sh	568 w,sh	
1309 m,sh		
1403 m,sh		
2280 s,sh		

[a] Room temperature.

[b] Room temperature.

[c] Low temperature.

Table 4A. Infrared spectrum of $WCl_4(CH_3CH_2CH_2CN)_2$

Near infrared, $\nu(cm^{-1})$[a]	Near infrared, $\nu(cm^{-1})$[a]	Far infrared, $\nu(cm^{-1})$[b]	Far infrared, $\nu(cm^{-1})$[c]
770 m,sh	1228 w,sh	134 m,br	264 w,br
818 w,sh	1250 w,br	150 m,br	279 w,br
839 m,sh	1320 w,sh	264 w,br	330 vs,vbr
873 s,sh	1330 s,vsh	325 vs,vbr	393 m,sh
925 m,sh	1388 s,sh	395 m,sh	425 m,sh
1045 s,sh	1398 s,sh	426 m,sh	
1078 m,sh	2278 s,sh	580 w,br	
1099 m,sh			

[a] Room temperature.

[b] Room temperature.

[c] Low temperature.

Table 5A. Infrared spectrum of $WCl_4[(C_2H_5)_2S]_2$

Near infrared, $\nu(cm^{-1})^a$	Near infrared, $\nu(cm^{-1})^a$	Far infrared $\nu(cm^{-1})^b$	Far infrared $\nu(cm^{-1})^c$
619 w,br	1104 m,sh	140 m,br	272 m,br
640 m,sh	1129 w,sh	154 m,br	326 vs,vbr
771 s,sh	1238 m,sh	210 w,br	395 w,sh
1022 s,sh	1261 s,sh	275 vw,br	Far infrared $\nu(cm^{-1})^d$
1076 w,sh	1279 m,sh	325 vs,vbr	
1091 w,sh	1419 s,br		
			130 s,br
			157 m,sh
			272 w,br
			330 vs,vbr

[a] Room temperature.

[b] Room temperature.

[c] Low temperature.

[d] Benzene solution.

Table 6A. Infrared spectrum of $WCl_4(C_4H_8S)_2$

Near infrared, $\nu(cm^{-1})^a$	Far infrared, $\nu(cm^{-1})^b$	Far infrared, $\nu(cm^{-1})^c$	Far infrared, $\nu(cm^{-1})^d$
612 w,br	106 w,br	256 m,sh	130 w,br
663 s,sh	129 s,br	272 m,sh	158 m,sh
759 s,sh	156 s,sh	323 s,br	264 w,br
880 s,sh	262 s,vbr	475 m,sh	327 s,sh
892 m,vsh	325 vs,vbr		478 m,sh
956 m,sh			524 s,sh
1040 w,br			
1081 m,sh			
1090 m,sh			
1131 w,sh			
1200 w,br			
1254 s,sh			
1267 s,sh			
1308 s,sh			
1329 w,sh			
1358 s,sh			
1390 s,sh			

[a] Room temperature.

[b] Room temperature.

[c] Low temperature.

[d] Tetrahydrothiophene solution.

Table 7A. Infrared spectrum of $WCl_4[P(C_6H_5)_3]_2$

Near infrared, $\nu(cm^{-1})^a$	Near infrared, $\nu(cm^{-1})^a$	Far infrared, $\nu(cm^{-1})^b$	Far infrared, $\nu(cm^{-1})^c$
626 w,br	999 s,vsh	257 w,br	258 vw,br
700 s,sh	1030 m,sh	322 s,sh	279 w,br
745 vs,sh	1077 m,sh	436 m,sh	322 s,br
754 vs,sh	1094 s,sh	454 m,sh	430 w,br
844 w,sh	1160 m,sh	499 s,sh	455 s,sh
854 w,sh	1191 m,br	510 s,sh	496 s,sh
930 w,br	1317 w,br	527 s,sh	509 s,sh
954 w,br	1369 m,sh		520 s,sh

[a] Room temperature.

[b] Room temperature.

[c] Low temperature.

Table 8A. Infrared spectrum of $WCl_4(C_5H_5N)_2$(I)

Near infrared, $\nu(cm^{-1})^a$	Near infrared, $\nu(cm^{-1})^a$	Far infrared, $\nu(cm^{-1})^b$	Far infrared, $\nu(cm^{-1})^c$
652 m,br	1157 w,br	136 s,br	225 m,sh
700 s,br	1216 s,sh	166 s,sh	233 w,br
760 s,sh	1240 w,sh	194 m,sh	320 vs,br
805 w,br	1269 w,sh	221 m,br	448 m,sh
861 w,sh	1358 m,sh	325 vs,vbr	
941 w,sh	1449 vs,vsh	449 m,sh	
1012 s,sh	1486 s,sh		
1049 m,sh	1569 w,sh		
1064 s,sh	1609 s,sh		
1090 w,br	1667 w,br		

[a] Room temperature.

[b] Room temperature.

[c] Low temperature.

Table 9A. Infrared spectrum of $WCl_4(C_5H_5N)_2$(II)

Near infrared, $\nu(\mathrm{cm}^{-1})^{a}$	Near infrared, $\nu(\mathrm{cm}^{-1})^{a}$	Far infrared $\nu(\mathrm{cm}^{-1})^{b}$	Far infrared $\nu(\mathrm{cm}^{-1})^{c}$
639 m,br	1160 w,sh	110 w,br	245 w,sh
700 m,br	1222 s,sh	124 w,br	253 w,sh
761 vs,vsh	1238 w,sh	130 w,br	265 w,sh
803 m,br	1252 m,br	136 w,br	278 m,br
875 w,sh	1366 m,sh	144 w,br	300 m,br
950 w,sh	1446 vs,sh	170 w,br	334 s,vbr
1014 s,sh	1490 s,sh	250 w,sh	400 w,sh
1047 m,sh	1532 w,sh	296 m,br	422 w,sh
1069 s,sh	1573 w,sh	336 vs,vbr	441 m,br
1090 w,br	1608 vs,sh	442 m,sh	
1114 w,br	1656 w,sh		

^{a}Room temperature.

^{b}Room temperature.

^{c}Low temperature.

Table 10A. Infrared spectrum of pyridine adduct(III)

Near infrared, $\nu(\mathrm{cm}^{-1})^{a}$	Near infrared, $\nu(\mathrm{cm}^{-1})^{a}$	Near infrared, $\nu(\mathrm{cm}^{-1})^{a}$	Far infrared $\nu(\mathrm{cm}^{-1})^{b}$
632 m,sh	1069 m,sh	1345 w,br	256 w,br
680 s,br	1095 w,br	1370 m,sh	299 s,br
697 s,sh	1112 w,br	1394 vs,sh	329 m,br
750 s,sh	1166 w,br	1488 s,sh	441 w,sh
763 m,sh	1198 w,br	1531 m,sh	
802 m,br	1223 s,sh	1607 s,sh	
1019 m,sh	1262 m,sh	1639 m,sh	
1048 m,sh	1328 w,br		

Table 11A. Infrared spectrum of WCl_4(bipy)

Near infrared, $\nu(cm^{-1})^a$	Near infrared, $\nu(cm^{-1})^a$	Far infrared $\nu(cm^{-1})^b$	Far infrared, $\nu(cm^{-1})^c$
645 m,sh	118 w,sh	130 m,vbr	306 s,br
657 m,sh	1155 w,sh	150 m,br	325 s,br
724 s,sh	1176 w,sh	203 m,sh	345 s,br
767 s,sh	1214 w,sh	212 w,br	
800 w,br	1233 w,br	307 s,br	
893 w,sh	1246 w,br	323 s,br	
973 w,sh	1271 vw,sh	331 s,br	
1006 w,sh	1316 m,sh	346 s,br	
1016 m,sh	1490 w,sh	423 m,sh	
1022 m,sh	1560 w,sh		
1045 w,sh	1597 m,sh		
1068 m,sh	1603 w,sh		

[a] Room temperature.

[b] Room temperature.

[c] Low temperature.

Table 12A. Magnetic susceptibility of Teflon

Temperature °K	$10^6 (\chi_g)$ emu/mole
33	-0.3655
40	-0.3549
49	-0.3614
58	-0.3522
72	-0.3615
81	-0.3650
100	-0.3601
121	-0.3626
141	-0.3673
160	-0.3661
181	-0.3630
255	-0.3707
297	-0.3672

Average value $(-.3637 \pm .0028)\text{x}10^{-6}$

Sample weight .3934 g

Table 13A. Magnetic susceptibilities of $WCl_4(CH_3CH_2CH_2CN)_2$

Temp. °K	$10^6(\chi_g)$ emu/gram	$10^6(\chi_M-\chi_D)$ emu/mole	Temp. °K	$10^6(\chi_g)$ emu/gram	$10^6(\chi_M-\chi_D)$ emu/mole
19	3.481	1842	83	3.430	1818
20	3.443	1824	90	3.422	1815
22	3.440	1824	99	3.446	1825
23	3.443	1824	112	3.430	1818
24	3.424	1815	125	3.426	1816
25	3.434	1820	140	3.405	1806
27	3.432	1822	153	3.361	1786
30	3.418	1812	169	3.309	1762
33	3.423	1814	186	3.326	1722
38	3.394	1801	201	3.148	1686
44	3.412	1810	223	3.032	1632
50	3.398	1803	242	2.876	1558
61	3.424	1815	261	2.808	1529
70	3.425	1815	286	2.707	1483
82	3.429	1818	287	2.714	1486

Sample mass = .1254 g

Molecular weight = 463.9 g

$\chi_D = -227\text{x}10^{-6}$ emu/mole

Table 14A. Magnetic susceptibilities of $WCl_4(C_4H_8S)_2$

Temp. °K	$10^6\chi_g$ emu/gram	$10^6(\chi_M-\chi_D)$ emu/mole	$10^6\chi_{corr}$ emu/mole
20	4.049	2283	2082
21	3.983	2250	2053
22	4.022	2270	2086
23	3.941	2229	2053
25	3.932	2224	2062
27	3.919	2218	2068
29	3.890	2203	2063
32	2.865	2190	2063
35	3.867	2192	2076
38	3.848	2183	2076
41	3.851	2157	2058
47	2.736	2126	2040
53	3.800	2159	2083
60	3.785	2151	2083
70	3.746	2131	2073
79	3.782	2149	2098
89	3.695	2106	2060
90	3.697	2107	2062
91	3.649	2083	2038
102	3.646	2072	2032
110	3.610	2062	2025
120	3.568	2042	2008
129	3.495	2005	1974
140	3.434	1975	1946
143	3.396	1956	1928
150	3.295	1905	1878
155	3.333	1924	1898
160	3.322	1918	1893
165	3.276	1896	1871
171	3.256	1885	1861
180	3.157	1836	1813
190	3.109	1812	1791
201	3.017	1765	1745
222	2.868	1691	1673
241	2.754	1633	1616
261	2.631	1571	1555
276	2.531	1521	1506
296	2.446	1479	1465

Sample mass = .0684 g. (20-90°K)
Sample mass = .1526 g (90- 296°K)
Molecular weight = 501.7 g/mole
$\chi_D = -252 \times 10^{-6}$ emu/mole

Table 15A. Magnetic susceptibilities of $WCl_4(C_5H_5N)_2(I)$

Temp. °K	$10^6\ \chi_g$ emu/gram	$10^6\ (\chi_M-\chi_D)$ emu/mole	$10^6\ \chi_{corr.}$ emu/mole
18	3.965	2147	1841
19	3.951	2139	1849
20	3.942	2135	1859
22	3.849	2090	1840
23	3.866	2098	1858
24	3.819	2076	1846
25	3.790	2062	1842
26	3.787	2060	1848
27	3.756	2046	1842
32	3.721	2029	1857
37	3.677	2007	1858
39	3.640	1989	1848
50	3.539	1941	1831
56	3.559	1950	1852
65	3.545	1944	1860
66	3.556	1949	1866
70	3.538	1940	1862
86	3.516	1929	1865
100	3.523	1933	1878
121	.3448	1887	1841
140	3.352	1850	1811
141	3.330	1839	1800
161	3.183	1768	1739
180	3.080	1718	1687
200	2.936	1649	1621
212	2.890	1626	1600
221	2.766	1567	1542
240	2.688	1530	1507
260	2.540	1457	1436
267	2.443	1410	1389
296	2.396	1388	1369
297	2.391	1385	1366

Sample mass = .0710 g

Molecular weight = 483.9 g/mole

$\chi_D = -228\times10^{-6}$ emu/mole

Table 16A. Magnetic susceptibility of $WCl_4[(C_2H_5)_2S]_2$

Temp. °K	10^6 χ_g emu/gram	$10^6(\chi_M-\chi_D)$ emu/mole	$10^6\chi_{corr}$ emu/mole
18	4.148	2356	1918
19	2.086	2330	1919
20	4.079	2327	1936
21	4.002	2299	1917
22	3.978	2276	1921
23	3.956	2265	1924
25	3.893	2232	1920
26	3.910	2241	1941
28	2.834	2203	1924
29	3.824	2197	1934
32	3.796	2183	1939
34	3.753	2162	1932
38	3.689	2129	1923
40	3.650	2110	1915
42	3.644	2107	1919
45	3.654	2112	1938
51	3.668	2119	1926
59	3.685	2127	1995
64	3.632	2101	1979
65	3.626	2098	1978
72	3.586	2077	1969
73	3.611	2090	1983
83	3.551	2040	1976
86	3.555	2062	1971
96	3.528	2048	1967
108	3.501	2035	1973
117	3.457	2012	1944
130	3.393	1980	1920
139	3.460	2015	1959
153	3.301	1933	1882
166	3.151	1858	1810
180	3.114	1839	1796
200	2.903	1732	1725
221	2.752	1656	1621
241	2.712	1635	1603
260	2.580	1568	1537
272	2.473	1515	1486
296	2.418	1487	1461

Sample mass = .1548 g

Molecular weight = 505.7 g/mole

$\chi_D = -264\times10^{-6}$ emu/mole

Table 17A. Magnetic susceptibilities of $WCl_4[(C_6H_5)_3P]_2$

Temp. °K	$10^6\ \chi_g$ emu/gram	$10^6(\chi_M-\chi_D)$ emu/mole	$10^6\ \chi_{corr}$ emu/mole
20	1.874	2074	1743
22	1.850	2054	1754
24	1.815	2024	1749
26	1.790	2001	1748
29	1.758	1975	1748
31	1.758	1975	1762
34	1.740	1959	1765
36	1.718	1940	1756
40	1.692	1917	1752
45	1.678	1905	1761
51	1.653	1884	1754
56	1.641	1874	1756
65	1.650	1881	1779
74	1.618	1855	1766
80	1.618	1854	1772
85	1.598	1837	1764
87	1.602	1840	1764
92	1.611	1842	1775
99	1.591	1830	1763
110	1.566	1809	1749
114	1.553	1797	1739
120	1.548	1793	1738
125	1.532	1780	1727
135	1.505	1757	1708
145	1.456	1715	1669
155	1.448	1708	1665
160	1.405	1671	1630
168	1.374	1644	1605
180	1.342	1616	1580
190	1.303	1584	1548
201	1.225	1516	1483
216	1.199	1495	1464
250	1.081	1392	1366
265	1.028	1347	1322
266	1.025	1344	1319
279	0.9590	1296	1271
297	0.9449	1275	1253

Weight sample = .1232 g

Molecular weight = 859.7 g/mole

$\chi_D = -463\times10^{-6}$ emu/mole

Table 18A. Magnetic susceptibilities of $WCl_4(Bipy)$

Temp. °K	$10^6(\chi_g)$ emu/gram	$10^6(\chi_M-\chi_D)$ emu/mole	μ_{eff} B.M.
19	6.500	3354	0.71
20	6.484	3346	0.73
21	6.423	3318	0.75
22	6.367	3290	0.76
23	6.297	3257	0.77
24	6.254	3236	0.79
25	6.129	3175	0.80
27	6.010	3118	0.82
29	5.884	3057	0.84
32	5.755	2995	0.88
35	5.487	2866	0.90
37	5.397	2823	0.91
39	5.299	2776	0.93
41	5.408	2828	0.96
42	5.398	2823	0.97
45	4.887	2577	0.96
50	4.723	2497	1.00
55	4.557	2417	1.03
60	4.382	2334	1.06
65	4.242	2266	1.09
70	4.075	2186	1.10
76	3.947	2114	1.15
85	3.875	2090	1.19
86	3.868	2086	1.20
96	3.613	1963	1.23
104	3.486	1802	1.26
115	3.325	1824	1.30
125	3.153	1741	1.32
135	3.047	1690	1.35
151	2.831	1586	1.38
166	2.608	1479	1.40
181	2.500	1427	1.44
201	2.314	1339	1.47
221	2.208	1286	1.51
241	2.109	1238	1.55
261	1.963	1168	1.56
280	1.821	1004	1.59
297	1.838	1107	1.62

Sample weight = 0.0992 g

Molecular weight = 481.9 g/mole

$\chi_D = -222\times10^{-6}$ emu/mole

Table 19A. Magnetic susceptibilities of $WCl_4(C_5H_5N)_2$(II)

Temp. °K	$10^6(\chi_g)$ emu/gram	$10^6(\chi_M - \chi_D)$ emu/mole	μ_{eff} B.M.
86	0.9852	704.8	0.70
87	0.8336	631.4	0.66
106	0.7858	608.2	0.72
107	0.8014	615.8	0.73
117	0.6741	554.2	0.72
124	0.6401	537.8	0.73
151	0.4704	455.6	0.74
175	0.3690	406.5	0.75
202	0.2893	368.0	0.77
225	0.2425	345.5	0.79
251	0.1823	316.2	0.80
294	0.1399	295.7	0.83
			0

Weight sample = 0.1002 g

Molecular weight = 483.9 g/mole

$\chi_D = -228\text{x}10^{-6}$ emu/mole

Table 20A. Experimental and calculated values of χ_{corr} $WCl_4(CH_3CH_2CH_2CN)_2$

Temp. °K	Experimental (10^6) emu/mole	Calculated[a] (10^6) emu/mole
20	1824	1817
25	1820	1817
30	1812	1817
50	1803	1817
60	1815	1817
70	1815	1817
80	1818	1817
90	1815	1816
100	1825	1815
110	1818	1814
125	1816	1808
140	1806	1798
155	1786	1783
170	1762	1760
185	1722	1731
200	1686	1695
225	1632	1620
240	1558	1568
260	1529	1490
285	1483	1383

[a] Parameters used: $\delta = 608\ cm^{-1}$; $\chi_1 = -7958 \times 10^{-6}$ emu/mole.

Table 21A. Experimental and calculated values of χ_{corr} $WCl_4(C_4H_8S)_2$

Temp. °K	Experimental (10^6) emu/mole	Calculated[a] (10^6) emu/mole
20	2082	2065
25	2062	2065
35	2076	2065
60	2083	2064
70	2073	2061
80	2098	2057
90	2062	2050
100	2032	2038
110	2025	2023
120	2008	2004
130	1974	1981
140	1946	1956
150	1878	1927
155	1898	1912
160	1893	1897
165	1871	1881
170	1861	1864
180	1813	1831
190	1791	1796
200	1745	1761
220	1673	1691
240	1616	1621
260	1555	1554
275	1506	1505
295	1465	1443

[a] Parameters used: $\delta = 348\ cm^{-1}$; $\chi_1 = -1.953 \times 10^{-3}$.

Table 22A. Experimental and calculated values of χ_{corr} $WCl_4(C_5H_5N)_2$

Temp. °K	Experimental (10^6) emu/mole	Calculated[a] (10^6) emu/mole
20	1851	1848
25	1842	1848
50	1831	1848
70	1862	1848
100	1878	1843
120	1841	1831
140	1805	1807
160	1739	1768
180	1687	1713
200	1621	1645
212	1600	1605
220	1564	1542
240	1507	1474
260	1436	1377
265	1389	1360
295	1369	1197

[a] Parameters used: $\delta = 525$ cm^{-1}; $\chi_1 = -7227 \times 10^{-6}$ emu/mole.

Table 23A. Experimental and calculated values of χ_{corr} $WCl_4[(C_6H_5)_3P]_2$

Temp. °K	Experimental (10^6) emu/mole	Calculated[a] (10^6) emu/mole
20	1743	1754
40	1752	1754
65	1779	1753
80	1772	1753
90	1775	1751
100	1763	1747
110	1749	1742
115	1739	1738
120	1738	1733
125	1727	1727
135	1708	1712
145	1669	1693
155	1665	1670
160	1630	1657
180	1580	1594
190	1548	1558
200	1517	1483
215	1464	1451
250	1366	1276
265	1322	1196
280	1271	1114
295	1253	1030

[a] Parameters used: $\delta = 506\ cm^{-1}$; $\chi_1 = -7500 \times 10^{-6}$ emu/mole.

Table 24A. Experimental and calculated values of χ_{corr} $WCl_4[(C_2H_5)_2S]_2$

Temp. °K	Experimental (10^6) emu/mole	Calculated[a] (10^6) emu/mole
20	1936	1926
25	1920	1926
40	1915	1926
50	1926	1926
65	1978	1926
85	1971	1926
95	1967	1925
110	1973	1924
115	1944	1923
130	1920	1917
140	1959	1909
155	1882	1892
165	1810	1876
180	1796	1843
200	1725	1780
220	1621	1694
241	1603	1586
260	1537	1457
270	1486	1385
295	1461	1187

[a] Parameters used: $\delta = 710\ cm^{-1}$; $\chi_1 = -22.404 \times 10^{-3}$ emu/mole.