Contribution from Ames Laboratory–USAEC and the Department of Chemistry, Iowa State University, Ames, Iowa 50010

# Magnetic Properties of Low-Symmetry $d^2$ Octahedral Complexes. A Study of the Synthesis and Magnetic Susceptibilities of Some Six-Coordinate Tungsten(IV) Halide Complexes

MARGARET A. SCHAEFER KING and R. E. McCARLEY*

*Received November 20, 1972*

Convenient new syntheses of tungsten(IV) halide adducts with a variety of different donor ligands have been developed. The complexes of the type $WX_4L_2$ were determined to have the following geometric configurations from a study of infrared spectra in the W–X (X = Cl or Br) stretching region: cis with L = $CH_3CN$, $C_2H_5CN$, $(C_2H_5)_2S$; trans with L = $C_3H_7CN$, $C_4H_8S$, and $(C_6H_5)_3P$. Detailed study of the magnetic susceptibilities of the $WCl_4L_2$ complexes with L = $C_3H_7CN$, $(C_2H_5)_2S$, $C_4H_8S$, and $(C_6H_5)_3P$ over the range 18–300°K revealed the presence of impurities attributed to complexes of tungsten(V), which became evident in the data over the range 18–50°K. After correcting the susceptibility data for the contribution from the impurities it was found that at temperatures below *ca.* 120°K the susceptibilities were independent of temperature; above this temperature the susceptibilities decreased. A model where all electronic degeneracies of the $d^2$ systems are removed by the combined action of spin-orbit coupling and low-symmetry ligand field was used to parameterize the susceptibility data. Good agreement between the experimental susceptibilities and those calculated with the equation $\chi_M = (\chi_0 + \chi_1 e^{-\delta/kT})(1 + e^{-\delta/kT})^{-1}$ indicated only the lowest two electronic levels were populated below *ca.* 250°K. The energy differences between the first and second levels ($\delta$) were found in the range 350–650 $cm^{-1}$. Paramagnetic pmr shifts were observed for the more soluble complexes $WX_4(C_3H_7CN)_2$ (X = Cl, Br) and $WCl_4[S(C_2H_5)_2]_2$.

## Introduction

The magnetic properties of low-symmetry, six-coordinate complexes of transition metal ions with $d^2$ electron configuration have been poorly characterized in those cases where *both* spin-orbit interactions (as with 5d series metal ions) and the low-symmetry component of the ligand field are large.[1] Whereas $d^2$ complexes with very strong low-symmetry ligand field components may be expected and have been found to be diamagnetic, as for example in the oxo complexes $MoOX_2L_3$[2] and $WOX_2L_3$;[3] on the other hand those with weak low-symmetry components will exhibit paramagnetic, spin-triplet ground-state terms. The description or prediction of the magnetic susceptibility behavior for complexes where $\lambda L \cdot S$ is greater than or comparable to the low-symmetry potential $V_{LS}$ is especially difficult.[1] Such is the case with tungsten(IV) complexes of the type *cis*- or *trans*-$WX_4L_2$ which are the subject of this study. In principle the ground-state splitting of the octahedral $^3T_{1g}$ term under spin-orbit and low-symmetry perturbation can be understood from ligand field-group theoretical arguments.[4] However the magnitude of these splittings and the number or ordering of levels which are accessible within $kT$ will determine the susceptibility behavior over a range of temperature. Until the present time the magnetic susceptibilities of such complexes had not been examined in sufficient detail that the magnitude and temperature dependence of reported magnetic moments could be understood and applied in a useful way during characterization of new compounds.

Magnetic measurements on several tungsten(IV) halide adducts have been reported previously. Among the first of these were the results of Kennedy and Peacock,[5] who studied the pyridine adducts $WX_4(py)_2$ obtained from the reaction of pyridine with the salts $K_2WX_6$ (X = Cl, Br). These authors suggested that the compound $WCl_4(py)_2$ exhibited antiferromagnetic interactions with a Neel temperature occurring at *ca.* 100°K. Later measurements on these same compounds in this laboratory failed to confirm this behavior.[6] However the compounds were prepared differently, *viz.*, by means of direct reactions of liquid pyridine with the anhydrous tungsten(IV) or tungsten(V) halides. Our measurements were difficult to interpret because of poor reproducibility of the results from one batch of the compounds to another. We concluded that small amounts of paramagnetic impurities, such as tungsten(III) or -(V) complexes, were produced in the reactions. Blight and Kepert[7] more recently have contended that these reaction conditions ultimately lead to formation of tungsten(III) adducts $WCl_3(py)_2$, but we have been unable to confirm this.

Other adducts which have been prepared, and on which susceptibility measurements have been obtained, are $WX_4(RCN)_2$ (X = Cl, Br; R = $CH_3$, $C_2H_5$, $C_3H_7$),[8] $WX_4$(bipy) (X = Cl, Br),[9] $WCl_4$(biphos) (biphos = 1,2-bis(diphenylphosphino)ethane),[10] and a whole series of phosphine adducts $WX_4(PR_3)_2$.[3] At room temperature these compounds generally exhibited magnetic moments ($\mu_{eff}$) in the range 1.5–2.2 BM. In those cases where the susceptibility was measured at more than one temperature the data indicated Curie-Weiss behavior with very large values of the Weiss constant $\Theta$.

In view of the lack of definitive data on the magnetic properties of tungsten(IV) complexes it became the object of this study to prepare a variety of tungsten(IV) halide adducts, determine their geometric configuration through infrared spectroscopy, and measure the magnetic susceptibilities down to very low temperatures. In the course of this work convenient new methods for the synthesis of the adducts were developed.

## Experimental Section

The tungsten halide starting materials $WCl_5$, $WCl_4$, and $WBr_4$ were prepared by reduction of $WCl_6$ or $WBr_5$ with $W(CO)_6$.[11] The neat ligands and solvents acetonitrile, propionitrile, butyronitrile, chlorobenzene, dichloromethane, and chloroform were dried over Linde 4A molecular sieves, outgassed, and vacuum distilled onto

---

[1] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 6, 37 (1964).

[2] A. V. Butcher and J. Chatt, *J. Chem. Soc. A*, 2652 (1970).

[3] A. V. Butcher, J. Chatt, G. J. Leigh, and P. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1064 (1972).

[4] H. Kamimura, S. Koide, H. Sekiyama, and S. Sugano, *J. Phys. Soc. Jap.*, 15, 1264 (1960).

[5] C. D. Kennedy and R. D. Peacock, *J. Chem. Soc.*, 3392 (1963).

[6] T. M. Brown and R. E. McCarley, unpublished research.

[7] D. G. Blight and D. L. Kepert, *J. Chem. Soc. A*, 534 (1968).

[8] E. A. Allen, B. J. Brisdon, and G. W. A. Fowles, *J. Chem. Soc.*, 4531 (1964).

[9] C. Hull and M. H. B. Stiddard, *J. Chem. Soc. A*, 1633 (1966).

[10] P. M. Boorman, N. N. Greenwood, and M. A. Hildon, *J. Chem. Soc. A*, 2652 (1970).

freshly outgassed molecular sieves for storage. Benzene was refluxed over sodium, outgassed, and stored over $Nb_2Cl_{10}$. The alkyl sulfide reagents ethyl sulfide and tetrahydrothiophene were dried, outgassed, and stored over $LiAlH_4$. All subsequent distillations and manipulations of these solvents and other reagents were performed on the high-vacuum manifold or in a drybox maintained under inert atmosphere at a dew point of *ca.* −78°.

**Preparation of Bis(ethyl sulfide)tetrachlorotungsten(IV).** Ethyl sulfide was found to react directly with $WCl_4$[11] by stirring the neat ligand with the solid halide at 50–60° for 12 hr. The product was recovered, after removal of ethyl sulfide, by extraction and crystallization from dichloromethane or benzene. Red-orange crystals of the compound were soluble in chloroform, dichloromethane, benzene, toluene, and ethyl sulfide. *Anal.* Calcd for $WCl_4[S(C_2H_5)_2]_2$: W, 36.37; Cl, 28.04. Found: W, 36.45; Cl, 28.13; Cl/W, 4.01.

**Preparation of Bis(tetrahydrothiophene)tetrachlorotungsten(IV).** This compound was obtained by continuous extraction of $WCl_4$[11] with neat tetrahydrothiophene in a modified Soxhlet extractor adapted to vacuum-line operation. As the extraction proceeded over a 2-day period, the red crystalline product formed from the extracted solution. The crystalline product then was isolated upon removal of solvent by vacuum distillation. The compound is sparingly soluble in solvents such as benzene and dichloromethane but more soluble in tetrahydrothiophene. *Anal.* Calcd for $WCl_4(SC_4H_8)_2$: W, 36.66; Cl, 28.26; C, 19.12; H, 3.19. Found: W, 36.48; Cl, 28.02; C, 19.44; H, 3.05; Cl/W, 3.99.

**Attempted Preparation of Tungsten(IV) Bromide Adducts with Sulfide Ligands.** Attempts were made to obtain the analogous complexes $WBr_4L_2$ by reaction of $WBr_4$ with sulfide ligands. However with both ethyl sulfide and tetrahydrothiophene the products were oily solids which proved difficult to purify. Analyses of these materials gave low Br/W ratios, in the range 3.6–3.8, which indicated partial reduction of the metal by the ligands.

**Preparation of Bis(acetonitrile)tetrachlorotungsten(IV).** It was found that this compound could be prepared by several methods including (1) direct reaction between $WCl_4$ and neat acetonitrile at 50° (very slow), (2) reaction between $WCl_5$ and acetonitrile (50–60% yield in 1–2 hr), or (3) reduction of $WCl_5$ with $W(CO)_6$ in acetonitrile. The first method was too slow to be convenient, while the second method often provided products having Cl:W < 4 and apparently contained residual organic oxidation products from the acetonitrile.

The reaction which consistently gave the best product and yield was reduction of $WCl_5$ with $W(CO)_6$ in acetonitrile, according to the stoichiometry of the equation

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

A stoichiometric mixture of $WCl_5$ and $W(CO)_6$ was stirred at room temperature in acetonitrile for 12 hr with provision for escape of CO through a mercury bubbler. The product was washed repeatedly with acetonitrile to remove soluble side products and any unreacted $W(CO)_6$. The relatively insoluble red compound was recovered in 60–70% yield. *Anal.* Calcd for $WCl_4(CH_3CN)_2$: W, 45.09; Cl, 34.77. Found: W, 45.26; Cl, 34.82; Cl:W, 3.99.

**Preparation of Bis(propionitrile)tetrachlorotungsten(IV).** This compound was most easily prepared by direct reaction of propionitrile with $WCl_4$ at 50° for 24 hr. The complex was sufficiently soluble to permit extraction of the product away from unreacted $WCl_4$ in an extractor and recovery of the solid by subsequent removal of solvent on the vacuum line. *Anal.* Calcd for $WCl_4(C_2H_5CN)_2$: W, 42.21, Cl, 32.55. Found: W, 42.38; Cl, 32.26.

**Preparation of Bis(*n*-butyronitrile)tetrachlorotungsten(IV).** Synthesis of this compound by any reactions in neat butyronitrile proved unsatisfactory. The analytical data for products from such reactions indicated that the Cl:W ratios were satisfactory, but the butyronitrile:tungsten W ratios were usually high, in the range 2.1–2.2. This problem was avoided when the complex was prepared by allowing butyronitrile and $WCl_4[S(C_2H_5)_2]_2$ to react in a molar ratio somewhat less than 2:1 using dichloromethane as solvent. The less soluble butyronitrile complex separated as red needles on standing at room temperature. Unreacted $WCl_4[S(C_2H_5)_2]_2$ was easily removed by filtration and brief washing of the product with dichloromethane. A yield of 80–90% was obtained. This compound was soluble in benzene and butyronitrile, but only slightly soluble in chloroform or dichloromethane. *Anal.* Calcd for $WCl_4(C_3H_7CN)_2$: W, 39.63; Cl, 30.57. Found: W, 39.45; Cl, 30.57; Cl:W, 4.01.

**Preparation of Tungsten(IV) Bromide-Nitrile Adducts.** In contrast to the unsuccessful attempts to prepare sulfide adducts of $WBr_4$, the nitrile adducts were easily obtained. 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 other products of the reaction by washing extensively with acetonitrile. *Anal.* Calcd for $WBr_4(CH_3CN)_2$: W, 31.40; Br, 54.59; C, 8.20; H, 1.02. Found: W, 31.20; Br, 54.77; C, 8.49, H, 1.08.

Another method which proved useful in obtaining the same product was the reaction of $W(CO)_6$ with bromine in acetonitrile. The reaction was performed with stoichiometry according to the equation

$$W(CO)_6 + 2Br_2 + 2CH_3CN = WBr_4(CH_3CN)_2 + 6CO$$

At room temperature the reaction proceeded readily with vigorous evolution of carbon monoxide. A subsequent extraction of the insoluble product with acetonitrile removed side products. The yield based on $W(CO)_6$ was 70–80%. *Anal.* Found: W, 31.28; Br, 54.73.

The propionitrile and butyronitrile adducts of $WBr_4$ were prepared by displacement of acetonitrile from $WBr_4(CH_3CN)_2$ with the appropriate neat ligand. In the case of the black crystalline $WBr_4(C_3H_7CN)_2$ recovered from butyronitrile again a slightly high ligand:metal ratio was indicated. *Anal.* Calcd for $WBr_4(C_3H_7CN)_2$: W, 28.60; Br, 49.82. Found: W, 28.75; Br, 49.02.

**Preparation of Bis(triphenylphosphine)tetrachlorotungsten(IV).** This complex was prepared by mixing a chloroform solution of $WCl_4[S(C_2H_5)_2]_2$ with a slight excess of triphenylphosphine. The yellow solid was precipitated upon mixing, and excess triphenylphosphine was removed by washing with chloroform. *Anal.* Calcd for $WCl_4[P(C_6H_5)_3]_2$: Cl, 16.68; C, 50.86. Found: Cl, 16.59; C, 50.70.

**Infrared Spectra.** These spectra were recorded on the Beckman IR-7 and IR-11 spectrophotometers. Samples were prepared by mulling with mineral oil in the drybox and sealing the mull between NaCl, CsI, or polyethylene windows, depending on the wave number region to be examined. Spectra were obtained for some samples at *ca.* −196° using a low-temperature cell. The cell consisted of a liquid nitrogen reservoir in contact with a copper window holder which was fitted with a CsI window. The reservoir fit into an outer jacket equipped with two CsI windows which lined up with the inner window to give an unobstructed beam path. After placing a mulled sample on the inner window in the drybox, the cell was removed and evacuated through a stopcock in the outer jacket, and liquid nitrogen added to the reservoir. Actual sample temperature was not recorded during a run.

Solution spectra in the region 90–600 $cm^{-1}$ were taken in polyethylene cells with 0.1- or 0.2-mm path length. Solutions were prepared and transferred to the cells in the drybox. The cells were sealed by fusing the polyethylene neck on the cells with a soldering gun.

**Magnetic Resonance Spectra.** Pmr spectra were obtained on a 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 −100 to +100°. Solutions were prepared on the vacuum line, filtered into the nmr tube, and sealed under vacuum. Tetramethylsilane was added to the solutions as an internal standard.

**Magnetic Susceptibility Measurements.** Samples of *ca.* 100 mg were packed into small Teflon buckets of known weight and sealed in the drybox. After weighing, the sample was transferred to the magnetic balance chamber and the chamber was evacuated. Measurements of the susceptibilities were made on a Faraday balance as previously described.[12] However, a cryostat was added to the system for cooling of the sample down to liquid helium temperatures. In this system the lowest sample temperature which could be attained was 18°K. A heater and automatic temperature controller were contained in the system. Temperatures were measured with a calibrated copper–constantan thermocouple in the range 40–300°K, and with a copper–gold–0.07% iron thermocouple in the range 18–50°K.

## Results and Discussion

**Infrared Spectra and Configuration of Adducts.** The spectra in the region 500–4000 $cm^{-1}$ were typical only of the coordinated organic ligands and will not be discussed here in detail. The coordinated nitriles typically showed shifts of $\nu(C\equiv N)$ to frequencies 20–30 $cm^{-1}$ higher than in

---

(11) The method of preparation of $WCl_4$ was found to be especially important for the reactions reported here. For these reactions the $WCl_4$ obtained by reduction of $WCl_6$ or $WCl_5$ with $W(CO)_6$ was found to be uniquely suitable. A report on these syntheses of $WCl_4$ and $WBr_4$ will be published elsewhere.

(12) J. G. Converse and R. E. McCarley, *Inorg. Chem.*, 9, 1361 (1970).

Table I. Infrared Spectra of $WX_4L_2$ Complexes in the Region 200-500 $cm^{-1}$

| | | Absorption maxima,[b] $cm^{-1}$ | |
|---|---|---|---|
| Compd | Temp[a] | ν(M-X) | Other (unassigned) |
| $WCl_4(CH_3CN)_2$ (mull) | RT | 284 m, 325 vs | 418 m, 428 m (δ(C-C-N))<br>235 s (unassigned) |
| | −196° | 289 m, 320 s, 337 s | 425 m, 435 m (δ(C-C-N))<br>237 m, 245 w (unassigned) |
| $WBr_4(CH_3CN)_2$ (mull) | RT | 216 vs, 245 vs | 425 m, 435 m (δ(C-C-N))<br>283 (unassigned) |
| | −196° | 218 vs, 242 vs, 250 s | 426 m, 436 m (δ(C-C-N))<br>287 w (unassigned) |
| $WCl_4(C_2H_5CN)_2$ (mull) | RT | 330 vs | 426 m (δ(C-C-N))<br>265 (unassigned) |
| | −196° | 327 s, 345 s | 428 w (δ(C-C-N))<br>268 w (unassigned) |
| $WCl_4(C_3H_7CN)_2$ (mull) | RT | 330 vs | 395 m, 426 m (δ(C-C-N))<br>264 w (unassigned) |
| | −196° | 330 vs | 393 s, 425 s (δ(C-C-N))<br>264 (unassigned) |
| $WCl_4[S(C_2H_5)_2]_2$ (mull) | RT | 325 vs, vbr | 275 w, 395 w (unassigned) |
| | −196° | 326 vs, vbr | 272 m, 395 w (unassigned) |
| $WCl_4[S(C_2H_5)_2]_2$ (soln[c]) | RT | 330 vs, vbr | 260 vw, 275 vw, 395 w (unassigned) |
| $WCl_4(SC_4H_8)_2$ (mull) | RT | 325 vs, vbr | 262 s, vbr, 472 m (unassigned) |
| | −196° | 323 s, br | 256 m, 272 m, 475 m (unassigned) |
| $WCl_4(SC_4H_8)_2$ (soln[d]) | RT | 327 s (sharp) | 264 w, 480 s (unassigned) |
| $WCl_4[P(C_6H_5)_3]_2$ | RT | 322 s, br | 257 w, 436 m, 454 m, 499 s (unassigned) |
| | −196° | 322 s, br | 258 vw, 279 w, 430 w, 455 s, 496 s (unassigned) |

[a] Only nominal temperatures indicated; actual temperatures not measured. RT = room temperature. [b] Band intensities indicated by v (very), s (strong), m (medium), w (weak), and br (broad). [c] Solution in benzene. [d] Solution in tetrahydrothiophene.

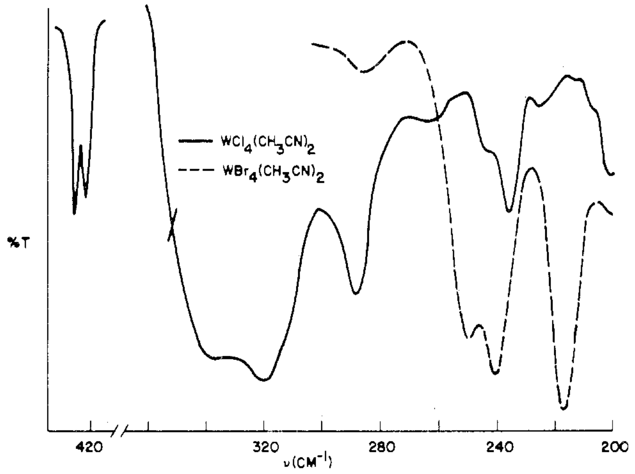

**Figure 1.** Low-temperature infrared mull spectra of acetonitrile adducts in the W–X (X = Cl, Br) stretching region.

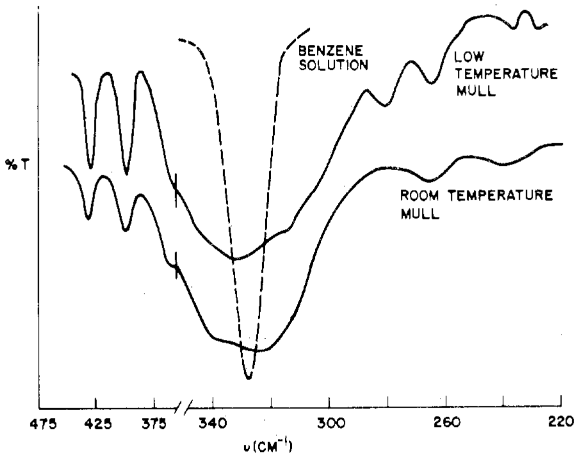

**Figure 2.** Infrared spectra of $WCl_4(C_3H_7CN)_2$ in mull and in benzene solution over the W–Cl stretching region.

the free nitrile, which is typical of nitriles when the M–N σ bond is established.[13] In the tetrahydrothiophene adduct $WCl_4(SC_4H_8)_2$ the C–S ring stretching mode, which occurs in the free ligand at 685 $cm^{-1}$, is shifted to 663 $cm^{-1}$; this decrease in frequency has been observed in other tetrahydrothiophene complexes.[14]

Spectra in the region 90-400 $cm^{-1}$ include the bands arising from metal-halogen (M-X) and metal-ligand (M-L) stretching modes. The bands arising from M-X stretching modes were used to ascertain the geometric configuration of the complexes. For adducts with the trans configuration (approximate $D_{4h}$ symmetry) only one infrared-active mode ($E_u$) is expected, whereas for the cis configuration ($C_{2v}$) four modes are expected ($2\ A_1 + B_1 + B_2$). Data in this region of the infrared spectra are summarized in Table I.

Inference of the correct configuration of the complexes was facilitated considerably by comparison of the room-temperature mull spectra with mull spectra taken at low temperature or spectra of solutions. The mull spectra of $WCl_4(CH_3CN)_2$ and $WBr_4(CH_3CN)_2$ taken at liquid nitrogen temperature are shown in Figure 1. In each spectrum the three most intense bands are readily identified as the M-X stretching modes of complexes with cis configuration. Corresponding data for $WCl_4(C_2H_5CN)_2$ clearly indicate this also is a cis complex. As shown in Figure 2 an unambiguous identification of the configuration of $WCl_4(C_3H_7CN)_2$ could not be made from the mull spectra; the low-temperature spectrum was not significantly improved over the room-tempera-

---

(13) K. F. Purcell and R. S. Drago, *J. Amer. Chem. Soc.*, **88**, 919 (1966).

(14) J. R. Alkins and P. J. Hendra, *Spectrochim. Acta*, **22**, 2075 (1966).

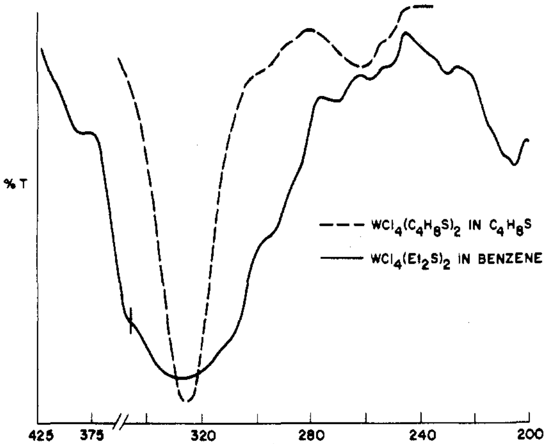

**Figure 3.** Infrared spectra of solutions of tungsten(IV) chloride-alkyl sulfide adducts in the W-Cl stretching region.

ture spectrum. However the solution spectrum of the butyronitrile adduct in benzene exhibited only one sharp band at 330 cm$^{-1}$ which was readily assigned to the trans configuration. Apparently considerable broadening of the single M-X stretching band results in the solid because of low site symmetry, as evidenced by the lack of sharpening of the spectrum at low temperature.

Again in the case of the sulfide adducts the mull spectra, even at low temperature, did not unambiguously define the configuration. However the solution spectra of $WCl_4[S(C_2H_5)_2]_2$ and $WCl_4(SC_4H_8)_2$ in benzene and tetrahydrothiophene, respectively, indicate the configurations cis for the former and trans for the latter. These solution spectra are shown in Figure 3, where it is evident that in the M-X stretching region the intense band of $WCl_4[S(C_2H_5)_2]_2$ consists of several overlapping, poorly resolved components, while the band of $WCl_4(SC_4H_8)_2$ consists of a single component typical of a trans complex. The spectrum of $WCl_4[P(C_6H_5)_3]_2$ clearly indicates the trans configuration, in agreement with previous work.[3]

A summary of the assigned configurations of the various adducts is given in Table II. The configurations adopted apparently are not determined solely by steric requirements of the ligands; otherwise the ethyl sulfide adduct might be expected to adopt the trans structure in keeping with its greater steric requirement compared to tetrahydrothiophene. Also it is not evident why the butyronitrile complex should adopt the trans structure unless interactions between adjacent ligand alkyl groups far removed from the metal atom become dominant for chains of three or more carbon atoms. The acetonitrile, propionitrile, tetrahydrothiophene, and triphenylphosphine complexes all adopt the configuration predicted on the basis of the model proposed by Zahrobsky for similar complexes of Sn(IV).[15]

**Table II.** Assigned Geometric Configurations of Tungsten(IV) Halide Adducts Based on Infrared Spectra

| Cis | Trans |
|---|---|
| $WCl_4(CH_3CN)_2$ | $WCl_4(C_3H_7CN)_2$ |
| $WBr_4(CH_3CN)_2$ | $WCl_4(SC_4H_8)_2$ |
| $WCl_4(C_2H_5CN)_2$ | $WCl_4[P(C_6H_5)_3]_2$ |
| $WCl_4[S(C_2H_5)_2]_2$ | |

**Magnetic Susceptibilities.** Measurements over the range 20-300°K were made on complexes $WCl_4L_2$ with L = butyronitrile, pyridine, 2,2′-bipyridine, ethyl sulfide, tetrahydrothiophene, and triphenylphosphine. A discussion of the results for the pyridine and bipyridine complexes is given in a separate paper[16] since the synthesis, structure, and properties of these complexes presented unusual difficulties, both in the experimental aspects and in interpretation of the results.

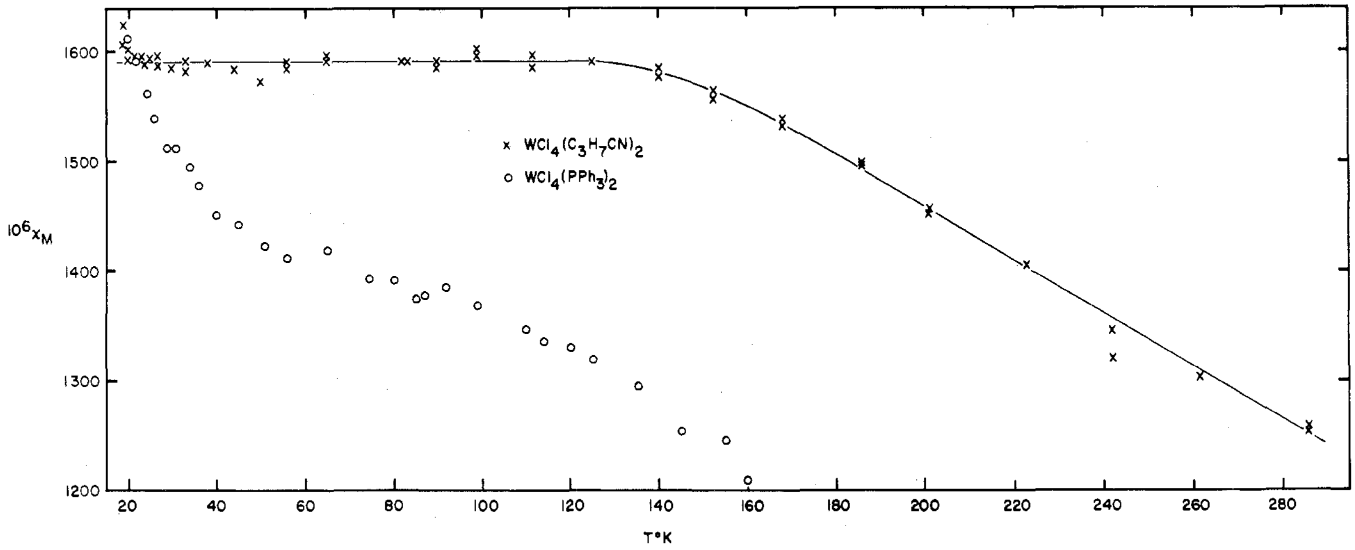

**Figure 4.** Magnetic susceptibilities of a pure tungsten(IV) halide adduct $WCl_4(C_3H_7CN)_2$ and an adduct containing some impurity with Curie temperature dependence $WCl_4[P(C_6H_5)_3]_2$.

Typical behavior of the magnetic susceptibilities as a function of temperature is illustrated for the butyronitrile and triphenylphosphine adducts in Figure 4. All of the complexes discussed here, except $WCl_4(C_3H_7CN)_2$, exhibit a region of nearly constant susceptibility over the range from about 50 to 120°K. Below 50°K all except the butyronitrile complex show rapidly increasing susceptibilities with decreasing temperature, and above about 120°K the susceptibilities begin to decrease with increasing temperature. However it is very important to note that the susceptibility of the butyronitrile complex remains constant from 120° down to the lowest temperatures attained. This behavior suggested that the rapidly increasing susceptibilities of the other complexes at the lowest temperatures were caused by traces of

---

(15) R. F. Zahrobsky, *J. Amer. Chem. Soc.*, **93**, 3313 (1971).

(16) M. A. S. King, J. G. Converse, T. M. Brown, and R. E. McCarley, to be submitted for publication.

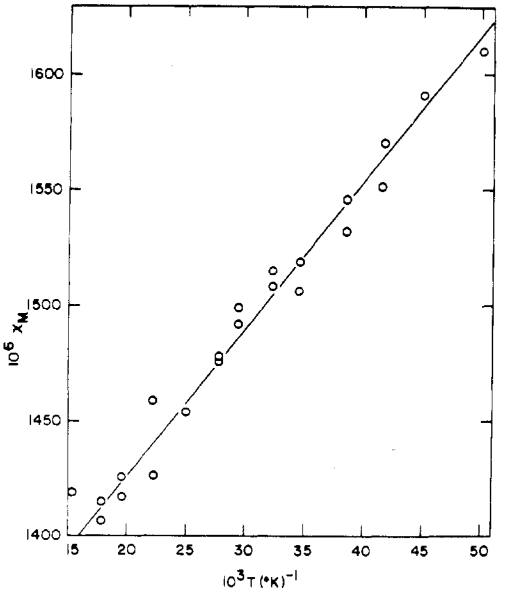

**Figure 5.** Curie plot of magnetic susceptibilities of $WCl_4[P(C_6H_5)_3]_2$ over the low-temperature range 20-60°K.

paramagnetic impurities which show normal Curie or Curie-Weiss temperature dependence. Hence the data were treated on this assumption by plotting $\chi_M$ *vs.* $1/T$ over the range 20-60°K as illustrated in Figure 5. For the complexes which showed this behavior *apparent* magnetic moments calculated from the slopes of the Curie plots were 0.18, 0.25, and 0.23 BM for $WCl_4(SC_4H_8)_2$, $WCl_4[S(C_2H_5)_2]_2$, and $WCl_4[P(C_6H_5)_3]_2$, respectively.

These small apparent moments probably arise from small amounts of tungsten(V) complexes present in the preparations, perhaps as $WOCl_3L_2$[17] of $WCl_5L_2$[18] adducts. An epr spectrum of $WCl_4[S(C_2H_5)_2]_2$ in toluene glass frozen at −196° revealed a weak anisotropic signal with $g_1 = 1.80$, $g_2 = 1.84$, and $g_3 = 1.87$. The average $g$ value of 1.84 is consistent with results reported for other tungsten(V) species,[19] but this value also compares well with an estimate of $g = 1.76$ for octahedral tungsten(III) with $g = 2(1 - 4\lambda/10Dq)$ and $\lambda = 600$ cm$^{-1}$, $10Dq = 20{,}000$ cm$^{-1}$. Thus the possibility of a tungsten(III) impurity cannot be excluded even though no well-characterized, paramagnetic complexes of tungsten(III) have been reported previously.

In order to correct for the presence of these paramagnetic impurities the apparent moments found for each complex were used to calculate corrected molar susceptibilities from the equations

$$\chi_{\text{impurity}} = N\beta^2\mu_{\text{app}}^2(3kT)^{-1} \qquad (1)$$

and

$$\chi_M^{\text{cor}} = \chi_M - \chi_D - \chi_{\text{impurity}} \qquad (2)$$

where $\mu_{\text{app}}$ is the apparent magnetic moment of the impurity derived from the Curie plots and $\chi_D$ is the standard atomic core diamagnetic correction. Since no impurity was detected in $WCl_4(C_3H_7CN)_2$ the last term of eq 2 was dropped in the calculation of $\chi_M^{\text{cor}}$ for this compound.

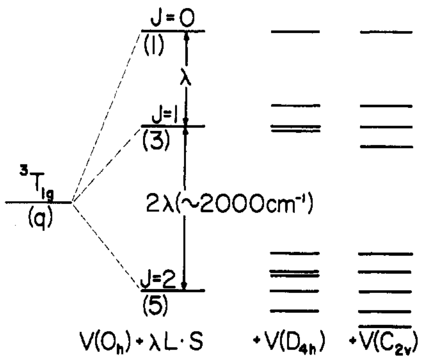

**Figure 6.** Schematic representation of energy level splittings of a six-coordinate d$^2$ transition metal ion with application of spin-orbit perturbation ($\lambda L\cdot S$) and low-symmetry ligand field potential $V(D_{4h})$ or $V(C_{2v})$.

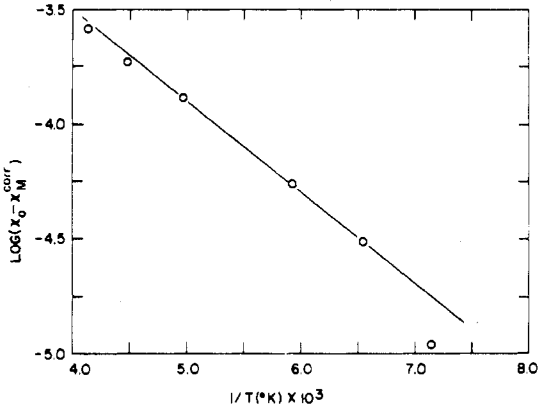

**Figure 7.** Plot of susceptibility data for $WCl_4(C_3H_7CN)_2$ over the range 120-250°K according to eq 6 for estimation of the parameters $\delta$ and $\chi_1$.

**Table III.** Magnetic Parameters Derived for $WCl_4L_2$ Complexes

| Complex | $10^6\chi_0$, emu/mol | $10^3\chi_1$, emu/mol | $\delta$, cm$^{-1}$ |
|---|---|---|---|
| $WCl_4(C_3H_7CN)_2$ | 1817 | −7.96 ± 1.2 | 608 ± 17 |
| $WCl_4[S(C_2H_5)_2]_2$ | 1926 | −20.4 ± 12.3 | 642 ± 100 |
| $WCl_4(SC_4H_8)_2$ | 2065 | −1.95 ± 0.4 | 348 ± 12 |
| $WCl_4[P(C_6H_5)_3]_2$ | 1754 | −8.68 ± 3.0 | 506 ± 35 |

A model for treatment of the magnetic susceptibilities of these complexes is based on the combined action of spin-orbit coupling and ligand field potential. Assuming that $V_{\text{OCT}} > \lambda L\cdot S > V_{\text{LS}}$, where $V_{\text{OCT}}$ is the octahedral component and $V_{\text{LS}}$ is the low-symmetry component of the ligand field potential, the ground-term energy levels will be split as shown in Figure 6. The notable feature of these splittings is that all ($C_{2v}$) or nearly all ($D_{4h}$) of the degeneracies of the $J = 1$ and $J = 2$ states are removed by the low-symmetry ligand field potential. In the case where a *nondegenerate* level lies lowest and no other levels are thermally populated the susceptibility will arise only from the second-order Zeeman term and hence will be temperature independent. If other levels are populated with increasing temperature, the susceptibility will become temperature dependent. The exact form of the temperature dependence will depend upon the degeneracy of the next higher level. For the case where the next higher level also is nondegenerate

$$\chi_M^{\text{cor}} = (\chi_0 + \chi_1 e^{-\delta/kT})(1 + e^{-\delta/kT})^{-1} \qquad (3)$$

where $\chi_0$ is the susceptibility when only the lowest level is populated and $\chi_1$ is the susceptibility of the next higher level; $\delta$ is the energy difference between the two levels. For the

---

[17] P. C. Crouch, G. W. A. Fowles, P. R. Marshall, and R. A. Walton, *J. Chem. Soc. A*, 1634 (1968).

[18] T. M. Brown and B. Ruble, *Inorg. Chem.*, **6**, 1335 (1967); P. M. Boorman, N. N. Greenwood, M. A. Hilden, and R. V. Parish, *J. Chem. Soc. A*, 2002 (1968); P. M. Boorman, M. Islip, M. M. Reimer, and K. J. Reimer, *J. Chem. Soc., Dalton Trans.*, 890 (1972).

[19] H. Kon and N. E. Sharpless, *J. Phys. Chem.*, **70**, 105 (1966).

**Table IV.** Experimental and Calculated Susceptibilities of Tungsten(IV) Halide Complexes

| *T*, °K | $10^6(\chi_M - \chi_D)$, emu/mol | $10^6\chi_M^{cor}$(exptl), emu/mol | $10^6\chi_M$(calcd), emu/mol |
|---|---|---|---|
| | $WCl_4(C_3H_7CN)_2$ | | |
| 19 | 1842 | 1842 | 1817 |
| 20 | 1824 | 1824 | 1817 |
| 22 | 1824 | 1824 | 1817 |
| 23 | 1824 | 1824 | 1817 |
| 24 | 1815 | 1815 | 1817 |
| 25 | 1820 | 1820 | 1817 |
| 27 | 1822 | 1822 | 1817 |
| 30 | 1812 | 1812 | 1817 |
| 33 | 1814 | 1814 | 1817 |
| 38 | 1801 | 1801 | 1817 |
| 44 | 1810 | 1810 | 1817 |
| 50 | 1803 | 1803 | 1817 |
| 61 | 1815 | 1815 | 1817 |
| 70 | 1815 | 1815 | 1817 |
| 82 | 1818 | 1818 | 1817 |
| 83 | 1818 | 1818 | 1817 |
| 90 | 1815 | 1815 | 1816 |
| 99 | 1825 | 1825 | 1815 |
| 112 | 1818 | 1818 | 1814 |
| 125 | 1816 | 1816 | 1808 |
| 140 | 1806 | 1806 | 1798 |
| 153 | 1786 | 1786 | 1783 |
| 169 | 1762 | 1762 | 1760 |
| 186 | 1722 | 1722 | 1731 |
| 201 | 1686 | 1686 | 1695 |
| 223 | 1632 | 1632 | 1620 |
| 242 | 1558 | 1558 | 1568 |
| 261 | 1529 | 1529 | 1490 |
| 286 | 1483 | 1483 | 1383 |
| 287 | 1486 | 1486 | 1383 |
| | $WCl_4(SC_4H_8)_2$ | | |
| 20 | 2283 | 2082 | 2065 |
| 21 | 2250 | 2053 | 2065 |
| 22 | 2270 | 2086 | 2065 |
| 23 | 2229 | 2053 | 2065 |
| 25 | 2224 | 2062 | 2065 |
| 27 | 2218 | 2068 | 2065 |
| 29 | 2203 | 2063 | 2065 |
| 35 | 2192 | 2076 | 2065 |
| 41 | 2157 | 2058 | 2065 |
| 47 | 2126 | 2040 | 2065 |
| 60 | 2151 | 2083 | 2064 |
| 70 | 2131 | 2073 | 2061 |
| 79 | 2149 | 2098 | 2057 |
| 89 | 2106 | 2060 | 2050 |
| 90 | 2107 | 2062 | 2050 |
| 102 | 2072 | 2032 | 2038 |
| 110 | 2062 | 2025 | 2023 |
| 120 | 2042 | 2008 | 2004 |
| 129 | 2005 | 1974 | 1981 |
| 140 | 1975 | 1946 | 1956 |
| 150 | 1905 | 1878 | 1927 |
| 155 | 1924 | 1898 | 1912 |
| 160 | 1918 | 1893 | 1897 |
| 165 | 1896 | 1871 | 1881 |
| 171 | 1885 | 1861 | 1864 |
| 180 | 1836 | 1813 | 1831 |
| 190 | 1812 | 1791 | 1796 |
| 201 | 1765 | 1745 | 1761 |
| 222 | 1691 | 1673 | 1691 |
| 241 | 1633 | 1616 | 1620 |
| 261 | 1571 | 1555 | 1554 |
| 276 | 1521 | 1506 | 1505 |
| 296 | 1479 | 1465 | 1443 |
| | $WCl_4[S(C_2H_5)_2]_2$ | | |
| 18 | 2356 | 1918 | 1926 |
| 19 | 2330 | 1919 | 1926 |
| 20 | 2327 | 1936 | 1926 |
| 21 | 2299 | 1917 | 1926 |
| 22 | 2276 | 1921 | 1926 |
| 23 | 2265 | 1924 | 1926 |
| 25 | 2232 | 1920 | 1926 |
| 26 | 2241 | 1941 | 1926 |
| 28 | 2203 | 1924 | 1926 |
| 29 | 2197 | 1934 | 1926 |
| 32 | 2183 | 1939 | 1926 |
| 34 | 2162 | 1932 | 1926 |
| 38 | 2129 | 1923 | 1926 |
| 40 | 2110 | 1915 | 1926 |
| 45 | 2112 | 1938 | 1926 |
| 51 | 2119 | 1926 | 1926 |
| 59 | 2127 | 1995 | 1926 |
| 65 | 2098 | 1978 | 1926 |
| 73 | 2090 | 1983 | 1926 |
| 83 | 2040 | 1976 | 1926 |
| 96 | 2048 | 1967 | 1925 |
| 108 | 2035 | 1973 | 1924 |
| 117 | 2012 | 1944 | 1923 |
| 130 | 1980 | 1920 | 1917 |
| 139 | 2015 | 1959 | 1909 |
| 153 | 1933 | 1882 | 1892 |
| 166 | 1858 | 1810 | 1876 |
| 180 | 1839 | 1796 | 1843 |
| 200 | 1732 | 1725 | 1780 |
| 221 | 1656 | 1621 | 1694 |
| 241 | 1635 | 1603 | 1586 |
| 260 | 1568 | 1537 | 1457 |
| 272 | 1515 | 1486 | 1385 |
| 296 | 1487 | 1461 | 1187 |
| | $WCl_4[P(C_6H_5)_3]_2$ | | |
| 20 | 2074 | 1743 | 1754 |
| 22 | 2054 | 1754 | 1754 |
| 24 | 2024 | 1749 | 1754 |
| 26 | 2001 | 1748 | 1754 |
| 29 | 1975 | 1748 | 1754 |
| 31 | 1975 | 1762 | 1754 |
| 34 | 1959 | 1765 | 1754 |
| 36 | 1940 | 1756 | 1754 |
| 40 | 1917 | 1752 | 1754 |
| 45 | 1905 | 1761 | 1754 |
| 51 | 1884 | 1754 | 1754 |
| 56 | 1874 | 1756 | 1754 |
| 65 | 1881 | 1779 | 1753 |
| 80 | 1854 | 1772 | 1753 |
| 92 | 1842 | 1775 | 1751 |
| 99 | 1830 | 1763 | 1747 |
| 110 | 1809 | 1749 | 1742 |
| 115 | 1797 | 1739 | 1738 |
| 120 | 1793 | 1738 | 1733 |
| 125 | 1780 | 1727 | 1727 |
| 135 | 1757 | 1708 | 1712 |
| 145 | 1715 | 1669 | 1693 |
| 155 | 1708 | 1665 | 1670 |
| 160 | 1671 | 1630 | 1657 |
| 180 | 1616 | 1580 | 1594 |
| 190 | 1584 | 1548 | 1558 |
| 200 | 1516 | 1483 | 1483 |
| 215 | 1495 | 1464 | 1451 |
| 250 | 1392 | 1366 | 1276 |
| 265 | 1347 | 1322 | 1196 |
| 280 | 1296 | 1271 | 1114 |
| 295 | 1275 | 1253 | 1030 |

case where the next higher level is doubly degenerate (as is possible for the trans complexes)

$$\chi_M^{cor} = [\chi_0 + (aT^{-1} + b)e^{-\delta/kT}](1 + 2e^{-\delta/kT})^{-1} \qquad (4)$$

where *a* is a term arising from the first-order Zeeman splitting of the doubly degenerate level, and *b* is the second-order susceptibility arising from this level.

Because both cis and trans complexes appear to show essentially the same behavior of $\chi_M$ *vs.* *T*, we assume that only nondegenerate levels are being populated over the tem-

**Table V.** Proton Nmr Shifts for $WX_4(C_3H_7CN)_2$ (X = Cl, Br) in Deuteriobenzene

| | $\Delta\nu$, ppm | | |
|---|---|---|---|
| X | $CH_3$ | $\beta$-$CH_2$ | $\alpha$-$CH_2$ |
| Cl | +1.86 | +9.85 | Not obsd |
| Br | +1.18 | +9.05 | Not obsd |

perature range of this study. Thus the susceptibility data have been fitted to eq 3. Values for $\chi_0$ were obtained from the average susceptibility over the low-temperature range where the $\chi_M^{cor}$ values are temperature independent, *i.e.*, $\chi_M^{cor}(av) = \chi_0$. Initial estimates of $\delta$ and $\chi_1$ were obtained from a series expansion of $(1 + e^{-\delta/kT})^{-1}$ in eq 3 and dropping higher order terms to obtain

$$\chi_M^{cor} = \chi_0 - (\chi_0 - \chi_1)e^{-\delta/kT} \tag{5}$$

which can be rearranged to

$$\log (\chi_0 - \chi_M^{cor}) = \log (\chi_0 - \chi_1) - \delta/2.303kT \tag{6}$$

A plot of $\log (\chi_0 - \chi_M^{cor})$ *vs.* $T^{-1}$ then should give a straight line with slope $= -\delta/2.303k$ over the temperature range where higher order terms in the expansion of $(1 + e^{-\delta/kT})^{-1}$ may be neglected; initial values of $\chi_1$ also are obtained by inserting the values of $\delta$, $\chi_0$, and $\chi_M^{cor}$ in eq 5 and solving for $\chi_1$. The initial estimates then were used to begin a fit of the data to eq 3 by trial and error. The plot of the data for $WCl_4(C_3H_7CN)_2$ over the range 140-250°K according to eq 6 is shown in Figure 7. The final values for $\delta$, $\chi_0$, and $\chi_1$ for the four complexes are given in Table III.

Using the values of the parameters given in Table III a satisfactory comparison of $\chi_M^{cor}$(exptl) with $\chi_M$(calcd) is obtained up to 250°K, where the agreement is within 1-2%, as shown in Table IV. Above about 250°K the agreement becomes poor for all but the tetrahydrothiophene complex. The divergence of experimental and calculated susceptibilities may result from the onset of population of still another level at the higher temperatures. The good agreement below 250°K lends support to the model used to interpret the data.

The values for $\delta$ are surprisingly large and do not provide insight to bonding differences that might be expected to arise from the various donor atoms in these complexes. The ground-state splittings are sufficiently large that all of the complexes behave much alike. Needless to say with the complicated behavior observed here a complete understanding of the energy levels and susceptibilities from a theoretical approach will be difficult to achieve. A case in point is the negative values of $\chi_1$ derived from the data, which we cannot reasonably explain. The negative values of $\chi_1$ are the sole indication that the model may be inadequate, but until more detailed elucidation of the energies of the lowest levels is attained independently by other methods the model used here should prove useful. Magnetic susceptibilities of similar complexes of Mo(IV), Re(V), and Nb(III) or Ta(III) should exhibit similar behavior. However complexes of Mo(IV) or Nb(III) will exhibit smaller spin-orbit splittings and this may cause more levels to be spaced within a given increment of $kT$. Provisions for population of more than the lowest two levels would have to be incorporated into the model under these circumstances.

**Table VI.** Proton Nmr Shifts for $WCl_4[S(C_2H_5)_2]_2$

| | $\Delta\nu$, ppm | | |
|---|---|---|---|
| Temp, °C | $CH_3$ | $CH_2$ | Solvent |
| −40 | −7.18 | Not obsd | $CH_2Cl_2$ |
| −20 | −7.22 | Not obsd | |
| 0 | −7.18 | Not obsd | |
| 20 | −7.22 | +23.85 | |
| 34 | −6.62 | +18.33 | $C_6D_6$ |
| 40 | −6.62 | +19.03 | |
| 50 | −6.58 | +19.70 | |
| 60 | −6.52 | +20.70 | |
| 70 | −6.55 | +21.30 | |

**Proton Magnetic Resonance Spectra.** Only three of the compounds $WCl_4(C_3H_7CN)_2$, $WBr_4(C_3H_7CN)_2$, and $WCl_4[S(C_2H_5)_2]_2$ were sufficiently soluble to permit the recording of their pmr spectra. As observed previously[3,20] these d$^2$ tungsten complexes behave much like corresponding complexes of d$^4$ metal ions, *e.g.*, Re(III) and Os(IV), in that the electron spin relaxation rate for both even-electron systems must be much greater than the nuclear electron hyperfine interaction, and paramagnetic contact shifts of the proton resonances may be observed. Because of the limited solubility of most of the complexes in suitable nmr solvents an extensive study of these spectra was not made. The spectra of the butyronitrile complexes were obtained for solutions in $C_6D_6$ only at room temperature. A small amount of $C_6H_6$ in the solvent served as internal standard since TMS obscured one of the signals from the sample. The shifts reported in Table V are given as $\Delta\nu$ (ppm), defined as the difference between the shift of a proton resonance in the complex and the shift of the same proton resonance in the uncomplexed ligand measured in the same solvent. The observed signals were sharp for the $CH_3$ protons, but broadened for the $\beta$-$CH_2$ protons. The failure to observe a resonance for the $\alpha$-$CH_2$ protons probably was due to a still greater broadening of this signal and the relatively weak signals resulting from the low solubility.

The spectrum of $WCl_4[S(C_2H_5)_2]_2$ was observed over the range −40 to +20° in dichloromethane and from 34 to 70° in deuteriobenzene. The observed shifts are given in Table VI. An interesting feature of these shifts is the lack of temperature dependence of the methyl proton shifts and the increasing positive shift of the methylene protons with increasing temperature. Also signals for the methylene protons show a very strong dependence of band width on temperature, whereas the widths of the methyl proton signals are not affected to this degree. Thus the methyl proton resonance is approximately a 1:2:1 triplet, but even at the higher temperatures the expected splitting of the methylene resonance from the methyl protons is not resolved. The methylene proton resonance becomes too broad to observe at <20°.

It is likely that the dominant term which determines the shifts in the butyronitrile complexes is different from that in the ethyl sulfide complex. Because the observed shifts for both the methyl and $\beta$-methylene protons have the same sign in the nitrile adducts, the anisotropic terms in the shift equation probably are dominant. In the case of the ethyl sulfide complex the isotropic contact shift may be dominant as indicated by the alternating sign of the shift. Owing to possible electron delocalization in the W-S bonds *via* d$\pi$-d$\pi$ interactions a greater contribution from the isotropic contact term for the ethyl sulfide ligand does not seem unreasonable. This is consistent also with the proton contact shifts observed by Butcher, *et al.*,[3] for the organophosphine adducts of $WCl_4$, where large positive shifts were observed for $\alpha$-methylene protons and smaller negative shifts for $\beta$-methylene or methyl protons on the alkyl chains attached to phosphorus.

In view of the complicated behavior of the magnetic susceptibilities of these tungsten complexes a quantitative

---

(20) J. R. Moss and B. L. Shaw, *J. Chem. Soc. A*, 595 (1970).

description of the proton contact shifts will be very difficult to achieve. If the model used for interpretation of the magnetic susceptibilities is correct, the temperature dependence of contact shifts will be difficult to assess, especially near room temperature where the relative population of low-energy electronic levels may be changing rapidly. It probably is fortuitous that the proton contact shifts reported by Butcher, *et al.*,[3] and magnetic susceptibilities reported by the same authors show a $T^{-1}$ or $(T + \Theta)^{-1}$ temperature dependence.

**Registry No.** $WCl_4[S(C_2H_5)_2]_2$, 40354-86-7; $WCl_4(SC_4H_8)_2$, 40354-87-8; $WCl_4(CH_3CN)_2$, 40354-88-9; $WCl_4(C_2H_5CN)_2$, 40354-89-0; $WCl_4(C_3H_7CN)_2$, 40354-90-3; $WBr_4(CH_3CN)_2$, 40354-91-4; $WBr_4(C_3H_7CN)_2$, 12081-02-6; $WCl_4[P(C_6H_5)_3]_2$, 36151-25-4; $WCl_4$, 13470-13-8; $WCl_5$, 13470-14-9; $WBr_4$, 14055-81-3.

---

Contribution from the Department of Chemistry,
Memphis State University, Memphis, Tennessee 38152

# Transition Metal π Complexes. II. Reactions of π-Cycloheptatrienylmolybdenum Dicarbonyl Iodide with Chelating Group Va Ligands[1]

THOMAS W. BEALL and LARRY W. HOUK*

*Received January 12, 1973*

Reactions of π-cycloheptatrienylmolybdenum dicarbonyl iodide (I) with several potentially bidentate group Va ligands have led to the formation of five types of derivatives: $h^7$-$C_7H_7MoCO$(ligand)I, $h^3$-$C_7H_7Mo(CO)_2$(ligand)I, $[h^7\text{-}C_7H_7Mo(CO)_2(\text{ligand})]^+PF_6^-$, $[h^7\text{-}C_7H_7MoCO(\text{ligand})]^+PF_6^-$, and $h^7$-$C_7H_7Mo$(ligand)I. The interaction of the tritertiary chelating agent $CH_3C[CH_2P(C_6H_5)_2]_3$ (triphos) with $C_7H_7Mo(CO)_2I$ resulted in the isolation of the nonsaline $C_7H_7MoCO$(triphos)I and the ionic $[C_7H_7Mo(\text{triphos})]^+I^-$. Formulas and structures of the new complexes were ascertained from infrared and nmr spectral data.

## Introduction

In contrast to the numerous accounts of π-cyclopentadienylmetal carbonyl reactions with group Va tertiary and oligotertiary ligands that have been reported in the past 20 years,[2] the analogous chemistry of other π-bonded ring metal carbonyls has been much less studied. Moreover, although a few tertiary phosphine and phosphite complexes are contained in two previous papers,[1,3] no reports have appeared describing reactions of π-cycloheptatrienyl group VIb metal carbonyls with chelating Lewis base ligands.

In a modest attempt to fill this void and to contrast π-cyclopentadienyl- and π-cycloheptatrienylmetal carbonyl chemistry, we have investigated reactions of π-cycloheptatrienylmolybdenum dicarbonyl iodide with one group Va tridentate ligand and a variety of bidentate ligands.

## Experimental Section

Microanalyses and molecular weights were performed by M-H-W Laboratory, Garden City, Mich. Infrared spectra were recorded in methylene chloride solutions and KBr pellets on a Model 621 Perkin-Elmer spectrometer. Proton nmr spectra were taken on Varian Associates Model T-60 and HA-100 machines in chloroform-*d* and acetone-$d_6$ with tetramethylsilane and hexamethyldisiloxane as internal standards, respectively. Conductivity measurements were made on $10^{-3}$ *M* nitrobenzene solutions using an Industrial Instruments conductivity bridge, Model RC 16B2, and a cell with platinum electrodes. Melting points were taken in open capillaries and are uncorrected. Dry nitrogen was used routinely for deaeration of solvents, maintenance of an inert atmosphere over reaction mixtures, and admission to evacuated vessels.

**Reagents.** The ligands 1,2-bis(diphenylphosphino)ethane[4] (diphos), *cis*-1,2-bis(diphenylphosphino)ethylene[5] (*cis*-diphos), 1,2-bis(dimethylphosphino)ethane[6] (mdiphos), bis(diphenylstibino)methane[7] (distib), 2-(2-diphenylphosphinoethyl)pyridine[8] (pyphos), and 1,1,1-tris(diphenylphosphinomethyl)ethane[9] (triphos) were synthesized according to literature procedures. Chemicals obtained commercially were bis(diphenylarsino)methane (arsars) (Strem Chemicals, Inc., Danvers, Mass.), 1-diphenylphosphino-2-diphenylarsinoethane (phosars) (Pressure Chem. Co., Pittsburgh, Pa.), 2-vinylpyridine (Reilly Tar and Chemical Corp., New York, N. Y.), triphenylphosphine and triphenylstibine (M and T Chemical Co., Inc., Rahway, N. J.), α,α′-dipyridyl (Aldrich Chemical Co., Inc., Milwaukee, Wis.), and Florisil (60–100 mesh) used for column chromatography and *o*-phenanthroline (Fisher Scientific Co., Fair Lawn, N. J.). The metal carbonyl precursor $C_7H_7Mo(CO)_2I$ was prepared by a literature method.[10]

**Syntheses.** The basic synthetic procedure involved stirring equimolar amounts of $C_7H_7Mo(CO)_2I$ and ligand in benzene at either ambient or reflux temperatures. Lengths of the reaction periods (Table I) were determined by monitoring the ν(CO) stretching frequencies in the infrared spectra. Filtration and/or evaporation of the solvent resulted in solid residues which were purified by recrystallization from $CH_2Cl_2$–hexane mixtures. Iodide salts were converted to hexafluorophosphates by dissolution in acetone followed by the addition of $NH_4PF_6$ in water and the slow evaporation of acetone. The precipitated solid then was recrystallized from acetone–benzene. A few typical preparations are as follows.

**$C_7H_7Mo(CO)_2$(diphos)I.** Equimolar quantities of $C_7H_7Mo(CO)_2I$ and diphos were stirred at 25° in benzene for 24 hr. The solvent was evaporated (25°, 40 mm) and the product was recrystallized from $CH_2Cl_2$–hexane.

**$[C_7H_7Mo(CO)_2(\text{diphos})]^+PF_6^-$.** $C_7H_7Mo(CO)_2$(diphos)I (0.4 g) was dissolved in acetone (100 ml) and $NH_4PF_6$ (2 g) in water (100 ml) was added. After 2 hr of stirring at 25° the acetone was evaporated (25°, 40 mm), the solid was collected and redissolved in acetone, and $NH_4PF_6$ (2 g) in water was added. After two further

---

[1] Part I: T. W. Beall and L. W. Houk, *Inorg. Chem.*, 11, 915 (1972).

[2] Some references in addition to those in ref 1 include: R. B. King, K. H. Pannell, C. A. Eggers, and L. W. Houk, *Inorg. Chem.*, 7, 2353 (1968); R. B. King, L. W. Houk, and P. N. Kapoor, *ibid.*, 8, 1792 (1969); R. B. King, L. W. Houk, and K. H. Pannell, *ibid.*, 8, 1042 (1969); K. W. Barnett and D. W. Slocum, *J. Organometal. Chem.*, 44, 1 (1972).

[3] R. B. King, *Inorg. Chem.*, 2, 936 (1963).

[4] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

[5] A. M. Aguiar and D. Daigle, *J. Amer. Chem. Soc.*, 86, 2299 (1964).

[6] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 896 (1961).

[7] Y. Matsumura and R. Okawara, *J. Organometal. Chem.*, 25, 439 (1970).

[8] V. E. Uhlig and M. Maaser, *Z. Anorg. Allg. Chem.*, 344, 205 (1966).

[9] R. B. King, L. W. Houk, and K. H. Pannell, *Inorg. Chem.*, 8, 1042 (1969).

[10] D. J. Bertelli, Ph.D. Thesis, University of Washington, 1961.