with a similar structure to the $Re_3Cl_{12}^{3-}$ group, *i.e.*, $n = 5$ and $m = 2$. Our theory suggests that this is unlikely, and the proper elucidation of the structure will provide a useful test of this theory.

Consider now an adduct of $MoCl_4$ with oxygen donor atoms. The relevant N_{Mo} for such a coordination sphere cannot be specified *a priori* but is probably in the region 55–62 ev which is appropriate for most metal chlorides and oxides. It is then impossible for molybdenum(IV) to be surrounded by eight chlorine or oxygen atoms, unless some Mo–Cl or Mo–O bonds are unusually long. However, it is doubtful whether the term "eight-coordinate molybdenum(IV)" would have much significance in the latter case. The molybdenum(IV) tetrachloride–oxygen donor adducts so far reported appear to be six-coordinate. The occurrence of eight-coordinate fluoro- and cyanatomolybdates is no less than the proverbial exception to prove the rule. These molybdates usually contain an alkali element which is assigned a very low χ. The low internuclear repulsion exerted by the alkali offsets and allows higher repulsion by molybdenum with a high CN. Unusually high CN can be thus estimated in the simpler ternary halides.

Experimental Section

The preparation, purification, analysis, and handling of the materials followed conventional methods or those described in the text. Where appropriate, moisture and air were rigorously excluded. The product of molybdenum(IV) oxide and carbon tetrachloride at 250–300° ("molybdenum tetrachloride") was red-black needles soluble in carbon tetrachloride. The following percentages and oxidation numbers were found for four samples: (1) Cl, 62%; Mo, 38.9%; (2) Cl, 56.5%; Mo oxidation no., 5.6 (assuming 39% Mo); (3) oxidation no., 5.4; (4) oxidation no., 5.6. (The last two results are from assays on carbon tetrachloride solutions of the product.)

Molybdenum(IV) chloride was prepared by the reduction of molybdenum(V) chloride by refluxing benzene.[4] There is a tendency to produce carbonaceous by-products, and consequently this material was not obtained in a pure form. The product was a black powder completely insoluble in carbon tetrachloride. *Anal.* Calcd for Cl_4Mo: Cl, 59.6; Mo, 40.3. Found: Cl, 54.4; Mo, 37.4; Cl/Mo = 4.0; Mo oxidation no., 4.1.

Bis(*n*-propyl cyanide)molybdenum(IV) chloride appeared as red-brown needles from a mixture of molybdenum(V) chloride and *n*-propyl cyanide after 24 hr at room temperature. *Anal.* Calcd for $C_8H_{14}Cl_4N_2Mo$: Cl, 37.8; Mo, 25.5; Mo oxidation no., 4.0. Found: Cl, 37.3; Mo, 24.6; Mo oxidation no., 3.9.

Molybdenum(V) chloride was Molybdenum Climax material, resublimed.

Infrared spectroscopy was conducted in a Perkin-Elmer Model 21 double-beam spectrophotometer, with matched NaCl window cells of 0.15-cm path length.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
INDIANA UNIVERSITY, BLOOMINGTON, INDIANA 47401

The Reaction of $K_3W_2Cl_9$ with Pyridine and Its Homologs

BY R. SAILLANT, J. L. HAYDEN, AND R. A. D. WENTWORTH

Received March 13, 1967

The reaction of $K_3W_2Cl_9$ (obtained from an improved synthesis) with pyridine has been investigated. The only isolable product was the diamagnetic $W_2Cl_6(py)_4$. Similar products were obtained from reactions with 4-picoline and 4-isopropylpyridine. The structures are presumed to consist of two octahedra sharing a common edge, and result from the breaking of one bridge bond in the $W_2Cl_9^{3-}$ ion. In the reaction with 4-isopropylpyridine, two isomeric compounds have been isolated. The similarity of the electronic spectra of one of these with that of $W_2Cl_6(py)_4$ suggests that these have an identical skeletal arrangement. Similarly the spectrum of the other isomer compares favorably to the product obtained from the reaction of $K_3W_2Cl_9$ with 4-picoline. The electronic spectrum of the $W_2Cl_9^{3-}$ ion is briefly discussed.

Introduction

The $W_2Cl_9^{3-}$ ion, one of the simplest examples of a metal cluster, is known[1] to consist of two octahedra sharing a common trigonal face. This structure suggests that there may be reactions in which the peripheral halogen atoms are preferentially removed with respect to the bridging atoms. Indeed, Jonassen, Cantor, and Tarsey[2] reported the isolation of diamagnetic $W_2Cl_6(py)_3$ by the reaction of pyridine with the potassium salt of the binuclear ion. It was postulated that the bridging arrangement in this compound was identical with that within the $W_2Cl_9^{3-}$ ion.

This reaction would appear to belong to an important general class of reactions which can occur with metal cluster compounds, namely those which leave the bridging arrangement completely intact. A recent example of this type is the reaction of phenyldiethylphosphine with the trigonal cluster, Re_3Cl_9, to form Re_3Cl_6(phenyldiethylphosphine)$_3$. X-Ray analysis[3] confirmed the preservation of the Re_3Cl_9 ring system. Another general class of reactions would include those which proceed with partial destruction of the bridging arrangement. While polymeric metal halides are not metal clusters, some of their reactions fall within this category. For example $CrCl_3$, a substance consisting of infinite chains of octahedra sharing common trigonal faces, is reported[4] to react with alkylphosphines

---

(1) W. H. Watson, Jr., and J. Waser, *Acta Cryst.*, **11**, 689 (1958).

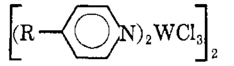
(2) H. B. Jonassen, S. Cantor, and A. R. Tarsey, *J. Am. Chem. Soc.*, **78**, 271 (1956).

(3) F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1094 (1964).

(4) K. Issleib and H. O. Fröhlich, *Z. Anorg. Allgem. Chem.*, **298**, 84 (1959).

to form $Cr_2Cl_6(R_3P)_4$. These compounds presumably consist of two octahedra sharing a common edge. Finally, there are those reactions which proceed with the complete destruction of the bridging arrangement. Examples of this type are well documented with metal carbonyls. In addition, $CrCl_3$ and $MoCl_3$ are reported to react with pyridine to form $CrCl_3(py)_3$[5] and $MoCl_3(py)_3$,[6] respectively.

The simplicity of the $W_2Cl_9^{3-}$ system lends itself to a study of the nature and scope of these three classes of reactions. This paper describes some of the reactions of this ion with heterocyclic organic bases to form



R = H, CH_3, and $(CH_3)_2CH$

Experimental Section

Materials.—4-Isopropylpyridine was kindly supplied by the Reilly Tar and Chemical Co. All other chemicals were reagent grade. Entirely equivalent results were obtained using both distilled and undistilled pyridines.

$K_3W_2Cl_9$.—Using the preparative methods of Heintz[7] and Laudise and Young,[8] the typical yields obtained in this laboratory for $K_3W_2Cl_9$ were 40% and less than 5%, respectively. By modifying Heintz's method, better yields were consistently obtained. The method is sufficiently different to warrant a full description.

To a mixture of 30 ml of H_2O and 30 g (0.22 mole) of K_2CO_3, 28 g (0.11 mole) of $WO_3 \cdot H_2O$ was added with stirring. The stirring was continued until a white slurry formed, and the mixture then was cooled to −20°. This mixture was then added dropwise with stirring to 600 ml of concentrated hydrochloric acid which had also been cooled to −20°. Simultaneously, gaseous HCl was bubbled slowly through the solution. During the last 30 min of the addition, four 25-ml portions of concentrated hydrochloric acid were added. After the addition of the tungstate solution was complete (*ca.* 90 min), another 100 ml of concentrated acid was added. The solution was removed from the coolant, allowed to stand for 30 min, and filtered. The filtrate was placed in a water bath at about 40° and 90 g of 200 mesh tin metal was slowly added over a period of about 75 min with continuous stirring. The color of the solution changed from blue, which occurred after the initial addition of tin, to deep wine-red and finally to a deep green. About 7 min after the appearance of the green color, the solution was placed in a Dry Ice–acetone bath and 1500 ml of absolute ethyl alcohol was immediately added. After the precipitation was complete, the mixture was filtered. The green product was then washed with absolute ethyl alcohol, followed by anhydrous ether. The yield at this point was generally about 70%. Recrystallization was accomplished by dissolving the product in a minimum quantity of dilute hydrochloric acid (*ca.* 0.5 *M*), filtering, cooling to −15°, and slowly saturating the solution with gaseous HCl. The green, crystalline product was washed as before. The yield is 60–62%. *Anal.* Calcd for $K_3W_2Cl_9$: W, 45.75; Cl, 39.70. Found: W, 45.30; Cl, 40.04.

The basic differences between this preparative scheme and that of Heintz are the lower reaction temperature, increased acidity, and the use of tin powder rather than foil. Increased yields were obtained by allowing the reaction to proceed at −20° without the addition of gaseous HCl; however, the best results were obtained by increasing the acidity at this temperature. The use of tin powder adds to the ease of addition, in contrast to difficulties encountered because of the obvious bulkiness of an equivalent quantity of tin foil. Furthermore, the increased surface area of the powder may well be an additional advantage.

Attempted Preparation of $W_2Cl_6(py)_3$.—Using the method of Jonassen, Cantor, and Tarsey,[2] 3.2 g of $K_3W_2Cl_9$ was refluxed for 6 hr in 150 ml of pyridine under nitrogen. The course of the reaction appeared to be identical with that described. A sample of the brown powder which resulted from the addition of ether to the cooled and filtered solution was redissolved in pyridine, precipitated by another addition of ether, and dried *in vacuo*. *Anal.* Calcd for $W_2Cl_6C_{15}H_{15}N_3$: Cl, 26.0; W, 45.0. Found: Cl, 21.35; W, 35.52. Another sample of the original brown powder was redissolved in pyridine and the solution was allowed to evaporate nearly to dryness. The resulting brown powder was washed and dried as before. *Anal.* Found: Cl, 19.95; W, 29.80.

$W_2Cl_6(py)_4$ and Solvates.—Freshly recrystallized $K_3W_2Cl_9$ (3.5 g) was added to 50 ml of cool pyridine, which had been previously refluxed under nitrogen for several hours. The reaction mixture was refluxed under nitrogen for 2.5 hr. The solution was then chilled and filtered. This product consisted of many small crystals and a red-brown material. The addition of ether to the filtrate produced an immediate brown precipitate. Recrystallization from CH_2Cl_2 gave diamagnetic $W_2Cl_6(py)_4$ as fine brown needles. *Anal.* Calcd for $W_2Cl_6C_{20}H_{20}N_4$: C, 26.81; H, 2.25; Cl, 23.75; W, 41.75. Found: C, 26.28; H, 2.75; Cl, 23.55; W, 41.15. Molecular weight determinations in $CHCl_3$ gave 785 (2.06×10^{-3} *M*) and 971 (2.58×10^{-3} *M*) which are to be compared to the theoretical 897. When the solid material which was originally obtained from the reaction mixture was extracted with CH_2Cl_2, the crystals dissolved and $W_2Cl_6(py)_4$ crystallized from the solution.

The infrared spectrum is tabulated in Table I. The frequencies of the bands between 1150 and 1600 cm^{-1} are typical[9] of coordinated pyridine.

TABLE I

INFRARED SPECTRA

Band maxima, cm^{-1} [a]

$W_2Cl_6(py)_4$

3020 w, 1600 s, 1480 m, 1360 w, 1220 s, 1155 m, 1065 s, 1045 m, 1010 m, 970 w, 815 w, 755 s, 682 s

$W_2Cl_6(4\text{-pic})_4 \cdot 4\text{-pic}$

3000 m, 1600 s, 1480 m, 1420 s, 1380 sh, 1335 w, 1235 w, 1205 m, 1055 w, 1020 s, 990 sh, 858 m, 805 s, 787 sh, 710 m

$W_2Cl_6(4\text{-ippy})_4$[b]

2900 m, 1610 s, 1485 m, 1450 w, 1420 s, 1380 w, 1360 w, 1300 m, 1220 m, 1090 w, 1050 m, 1015 m, 950 w, 930 w, 890 m, 825 s, 760 m

[a] s, strong; m, medium; w, weak; sh, shoulder. All spectra were taken using both Nujol mulls and KBr wafers. [b] The spectra for both the brown and red-brown isomers are identical.

Recrystallization of the brown precipitate from acetonitrile yielded diamagnetic $W_2Cl_6(py)_4 \cdot CH_3CN$ as brown plates. *Anal.* Calcd for $W_2Cl_6C_{22}H_{23}N_5$: C, 28.17; H, 2.47; N, 7.47; Cl, 22.68; W, 39.21. Found: C, 28.13; H, 2.45; N, 7.35; Cl, 22.30; W, 39.25. The pmr spectra in $CDCl_3$ at high amplification showed a resonance at τ 8.0 which duplicates the value for free CH_3CN in the same solvent. The relative intensity of the signal with respect to the ring protons at much lower fields was 2.9:20. Heating the solid sample *in vacuo* with an infrared lamp resulted in the loss of the solvent molecule and yielded $W_2Cl_6(py)_4$. *Anal.* Found: Cl, 23.35. The resonance due to the CH_3 protons was no longer present in the pmr spectrum. In this and all subsequent experiments, prolonged heating resulted in no further change in the analytical results.

---

(5) P. Pheiffer, *Z. Anorg. Allgem. Chem.*, **56**, 97 (1907).

(6) A. Rosenheim, G. Abel, and R. Lewy, *ibid.*, **197**, 202 (1931).

(7) E. A. Heintz, *Inorg. Syn.*, **7**, 142 (1963).

(8) R. A. Laudise and R. C. Young, *ibid.*, **6**, 149 (1960).

(9) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961), and references therein.

Recrystallization of the brown precipitate from acetone produced diamagnetic $W_2Cl_6(py)_4 \cdot {}^2/_3(CH_3)_2CO$. *Anal.* Calcd for $W_2Cl_6C_{22}H_{24}N_5O_{0.67}$: C, 27.20; H, 2.57; Cl, 22.80; W, 39.35. Found: C, 27.40; H, 2.60; Cl, 22.50; W, 39.80. The pmr spectrum contained a resonance at τ 7.83, which duplicates the value for free acetone. The infrared spectrum contained a typical carbonyl band at 1710 cm^{-1}. After heating *in vacuo*, both of these signals disappeared and the spectrum of $W_2Cl_6(py)_4$ was produced. *Anal.* Found: Cl, 23.60.

$W_2Cl_6(4\text{-pic})_4 \cdot 4\text{-pic}$.—This compound was prepared analogously to $W_2Cl_6(py)_4$ by refluxing $K_3W_2Cl_9$ with 4-picoline for 3 hr. The mixture was cooled and filtered. The small, red-brown crystals, which appeared completely uniform under a microscope, were washed extensively with water, ethyl alcohol, and ether. The product was diamagnetic. *Anal.* Calcd for $W_2Cl_6C_{30}H_{35}N_5$: C, 34.45; H, 3.37; Cl, 20.33; W, 35.15. Found: C, 34.09; H, 3.22; Cl, 20.51; W, 35.18. Heating *in vacuo* produced $W_2Cl_6(4\text{-pic})_4$. *Anal.* Calcd: Cl, 22.23. Found: Cl, 21.95. These compounds are only slightly soluble in acetonitrile and chloroform and insoluble in other common organic solvents.

$W_2Cl_6(4\text{-ippy})_4$.—The method of preparation was similar to those given above. However, the 4-isopropylpyridine was held at 80°, rather than at reflux temperature. After 2.5 hr the solution was cooled and filtered. The red-brown powder was washed successively with water, ethyl alcohol, and ether. The product, after drying, was stirred extensively with benzene and then filtered. From the filtrate, brown crystals were obtained. The remainder of the solid product was dissolved in $CHCl_3$, from which red-brown crystals were obtained. Both products were diamagnetic. *Anal.* Calcd for $W_2Cl_6C_{32}H_{44}N_4$: C, 36.10; H, 4.13; N, 5.26; Cl, 20.00; W, 34.50. Found for the brown crystals: C, 36.33; H, 4.22; N, 5.22; Cl, 19.90; W, 33.65. Found for the red-brown crystals: C, 36.35; H, 4.23; N, 5.40; Cl, 19.82; W, 34.15. A molecular weight determination for the brown isomer in $CHCl_3$ gave 1040 (2.43×10^{-3} *M*), in good agreement with the calculated 1064. The relative insolubility of the red isomer prevented a similar measurement. In addition to their differing solubilities the chemical shifts of the methyl protons are slightly different. In $CDCl_3$, the characteristic doublet appears at τ 8.8 for the brown material and τ 8.9 for the red-brown product.

Reactions with 2-Picoline and 3-Picoline.—When methods similar to those described above were used, intractible, brown oils were obtained.

Instrumentation.—Infrared spectra (Table I) were recorded using a Perkin-Elmer Model 137 spectrophotometer, while the electronic spectra were obtained using a Cary Model 14 spectrophotometer. A Varian A-60 spectrometer was used to obtain the pmr spectra. TMS was used as an internal calibrant.

Molecular weights were determined by osmometry with a Mechrolab Model 301-A instrument. Because of solubility limitations, the results are believed to be reliable only to ±100 molecular weight units.

Magnetic susceptibilities were measured using an apparatus similar to that recently described by Hatfield, Fountain, and Whyman.[10]

Analyses.—Gravimetric analyses for tungsten were performed by oxidizing the sample with 6 *N* HNO_3, filtering the precipitated tungstic acid, and heating the product at 710° for 1 hr. Chloride analyses were obtained by potentiometric titration of samples which had been oxidized with 3 *N* HNO_3. Carbon, hydrogen, and nitrogen analyses were performed by Huffman Laboratories, Wheatridge, Colo.

Results and Discussion

General Properties of Compounds.—In the published procedure[2] for the preparation of $W_2Cl_6(py)_3$, $K_3W_2Cl_9$ is suspended in refluxing pyridine for 6 hr. In our hands, when this procedure was followed, the resulting brown powders gave analyses which were completely out of harmony with the required values. By decreasing the reaction time to 2.5 hr, diamagnetic, brown, crystalline compounds were obtained. Their exact composition depended upon the choice of solvent used for recrystallization, but in general was $W_2Cl_6(py)_4 \cdot n$(solvent) (acetonitrile, $n = 1$; acetone, $n = {}^2/_3$; and methylene chloride, $n = 0$). While their molar solubility in organic solvents is low, sufficient quantities could be dissolved to confirm the presence of the solvate molecules from the pmr spectra. Molecular weight determinations for $W_2Cl_6(py)_4$ indicated that the dimeric formulation was correct. Since the determination was obtained from solutions whose concentrations were less than those recommended for the instrument, some dissociation might not have been detected. However, solutions of this compound in chloroform follow the Beer–Lambert law at all wavelengths in the near-infrared, visible, and ultraviolet regions of the spectrum. Furthermore, its solutions in acetonitrile, as well as those of the solvates, are completely unreactive to $AgNO_3$, even after standing as long as 8 hr.

The solvent can be completely removed from each of the solvates by heating *in vacuo* to yield products whose infrared spectra were identical with that of $W_2Cl_6(py)_4$. In chloroform solutions that portion of their pmr spectra due to the solvent molecule appears at frequencies identical with those of the free solvent in chloroform. In addition the solvates are readily interconvertible by recrystallization from the appropriate solvent. These results are consistent with a structure in which the solvent molecule is not bound, or is only weakly bound, to a metal atom.

When $K_3W_2Cl_9$ was allowed to react with 4-picoline, red-brown $W_2Cl_6(4\text{-pic})_5$ was obtained. Its relative insolubility made it impossible to recrystallize. Upon grinding the odor of the organic base was noticeable, and, indeed, after heating *in vacuo* $W_2Cl_6(4\text{-pic})_4$ was obtained. Thus, it appears that the correct formulation of the original material is the solvate, $W_2Cl_6(4\text{-pic})_4 \cdot 4\text{-pic}$. Dilute solutions of this compound are also unreactive to $AgNO_3$.

Finally, the reaction of $K_3W_2Cl_9$ with 4-isopropylpyridine produced $W_2Cl_6(4\text{-ippy})_4$ in apparently two isomeric forms. While their infrared spectra are virtually identical, the near-ultraviolet spectrum of the red isomer is vastly different from that of the brown isomer. The experimental molecular weight for the brown isomer confirms the dimeric formulation. Unfortunately, the relative insolubility of the other isomer thwarted attempts to determine its molecular weight. However, the observed diamagnetism of this compound, as well as that of $W_2Cl_6(4\text{-pic})_4 \cdot 4\text{-pic}$, supports their assumed dimeric nature. Polymerization isomerization could provide an alternate explanation, but would seem unlikely in view of subsequent arguments.

The yields from these reactions are markedly dependent upon the history of the $K_3W_2Cl_9$, with best results being obtained from freshly recrystallized mate-

---

[10] W. E. Hatfield, C. S. Fountain, and R. Whyman, *Inorg. Chem.*, **5**, 1855 (1966).

rial. However, in any case, the products which have been characterized constitute only about 20% of the theoretical yield. The remainder generally consists of powders from which we have been unable to obtain any consistent analytical results, and it is not unlikely that $W_2Cl_6(py)_3$, if it exists, could be found in these. Furthermore, the shorter reaction times which have been used should favor products in which little or no destruction of the bridging arrangement has occurred.

Possible Structure and Isomers.—The electronic spectra of these compounds are tabulated in Table II and displayed in Figures 1 and 2. It is clear that there are present in the spectrum of each some features at lower wavenumbers which are remarkably similar to those found in the spectrum of the $W_2Cl_9^{3-}$ ion (Figure 1). According to the molecular orbital approach of Cotton and Haas[11] when applied to two octahedra sharing a common trigonal face, this resemblance might not be unexpected for the previously reported $W_2Cl_6(py)_3$, providing the bridging arrangement remains completely intact. However, for dinuclear compounds containing ten bound ligands, it is somewhat surprising since this stoichiometry would indicate the probability that only two bridged halogen atoms remain after the course of the reaction. Alternatively, the bridging arrangement may have remained intact so that four ligands are now bound on the periphery of one tungsten atom. However, the resulting increase in nonbonded repulsions would seem to render this model untenable. Thus, it would appear that the most probable structure[12] consists of two octahedra sharing a common edge (Figure 3). A similar structure has been proposed[4] for $Cr_2Cl_6(R_3P)_4$. The observed diamagnetism would then result from the overlap of the *xy*, *xz*, and *yz* orbitals on the adjacent metal atoms.

TABLE II

ELECTRONIC SPECTRA

Compound	Band maxima, $cm^{-1} \times 10^{-3}$ [a]
$W_2Cl_6(py)_4$[c]	11.8 (130),[b] 12.5 (178), 13.7 (340), 16.7 (880),[b] 20.8 (6300), 26.4 (11,000), 30.5 (12,500),[b] 34.0 (16,600)
$W_2Cl_6(4\text{-pic})_4 \cdot 4\text{-pic}$[d]	10.7 (65),[b] 12.8 (234), 14.0 (430), 16.3 (130),[b] 20.7 (5800), 24.4 (13,000), 25.6 (10,000),[b] 34.7 (8800), 38.5 (16,700)
$W_2Cl_6(4\text{-ippy})_4$[e] (brown isomer)	10.7 (72),[b] 12.5 (250),[b] 13.6 (430), 17.0 (660),[b] 20.7 (3700), 26.3 (6000), 31.5 (7700), 33.3 (8000)
$W_2Cl_6(4\text{-ippy})_4$[e] (red isomer)	11.3 (56),[b] 12.8 (230), 14.1 (470), 15.4 (118),[b] 17.0 (320),[b] 20.7 (10,250), 24.8 (20,800), 31.9 (10.700), 37.6 (37,000)
$K_3W_2Cl_9$[f]	13.2 (50), 15.9 (160), 21.9 (4730), 26.3 (120)[b]

[a] Molar extinction coefficients are given in parentheses. [b] Shoulder. [c] In CH_2Cl_2. [d] In CH_3CN. [e] In $CHCl_3$. [f] In H_2O.

This skeletal arrangement permits a large number of

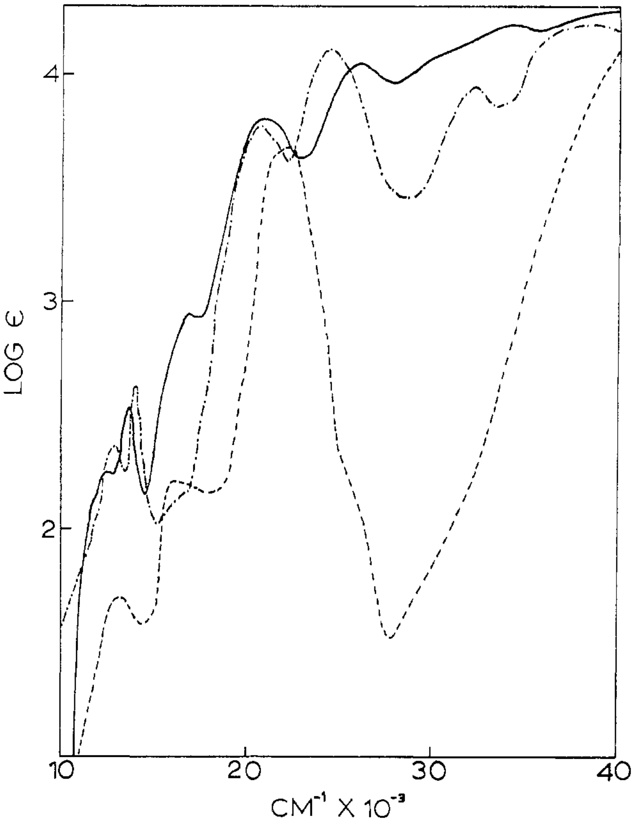


Figure 1.—Electronic spectra of compounds: ——— $W_2Cl_6(py)_4$; •—•—•— $W_2Cl_6(4\text{-pic})_4 \cdot 4\text{-pic}$; – – – – $K_3W_2Cl_9$.

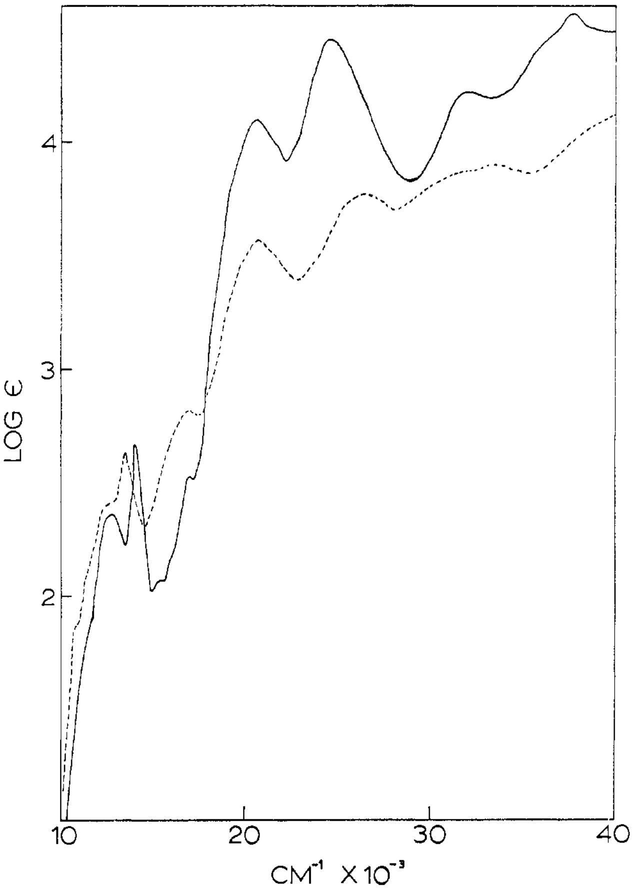


Figure 2.—Electronic spectra of the isomers of $W_2Cl_6(4\text{-ippy})_4$: ——— red-brown isomer; -------- brown isomer.

---

(11) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

(12) A referee has suggested an alternative structure, $(py)_2Cl_3WWCl_3(py)_2$, based on the structure of the rhenium dimers which contain no chlorine bridges. See for example, F. A. Cotton, C. Oldham, and R. A. Walton, *ibid.*, **6**, 214 (1967). While our experimental data cannot rule out this possibility, it would certainly require a much greater rearrangement of the atoms within the dimer than the skeletal arrangement shown in Figure 3.

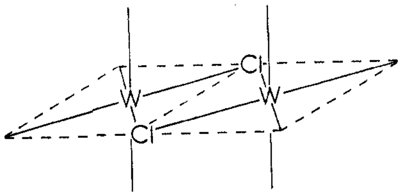


Figure 3.—Proposed skeletal arrangement of $W_2Cl_6(py)_4$ and analogous compounds.

isomers, but only in the case of W_2Cl_6(4-ippy)$_4$ have isomeric forms been successfully demonstrated. However a close inspection of Figures 1 and 2 will reveal that there exists a striking similarity in the electronic spectrum of the brown form of that compound with that of the brown form of $W_2Cl_6(py)_4$. Similarly, the spectrum of the red-brown isomer compares very favorably to that of the red-brown form of W_2Cl_6(4-pic)$_4$·4-pic. The similarity in the ultraviolet region of the spectrum is dramatically demonstrated in Figure 4. Furthermore, the brown compounds display a greater solubility than their red counterparts. It seems altogether reasonable, then, that the brown forms of W_2Cl_6(4-ippy)$_4$ and $W_2Cl_6(py)_4$ have similar structures, as do the red-brown forms of W_2Cl_6(4-ippy)$_4$ and W_2Cl_6(4-pic)$_4$.

The Spectrum of $K_3W_2Cl_9$.—The electronic spectrum of $K_3W_2Cl_9$ (Table II and Figure 1) in aqueous solutions appears to be in good agreement with that published by König,[13] who unfortunately did not include the exact wavenumbers of the band maxima nor their molar extinction coefficients. The latter are considerably greater than those given by Jørgensen,[14] who measured the spectrum of the $W_2Cl_9^{3-}$ produced in solution by reduction of W(VI) with zinc amalgam. Because of the low intensity of the bands at 13,200 and 15,900 cm^{-1}, Jørgensen assumed that these absorptions were due to the $^4A_2 \rightarrow {}^2E$ and $^4A_2 \rightarrow {}^2T_2$ transitions within the individual chromophores. It is now clear that these assignments are not valid. Furthermore, since the absorptions appear at much lower wavenumbers than would be predicted for the unknown WCl_6^{3-}, they probably do not represent spin-allowed transitions within the individual chromophores. The most reasonable explanation is that they are transitions between d orbitals which are extensively delocalized between the two metal atoms.

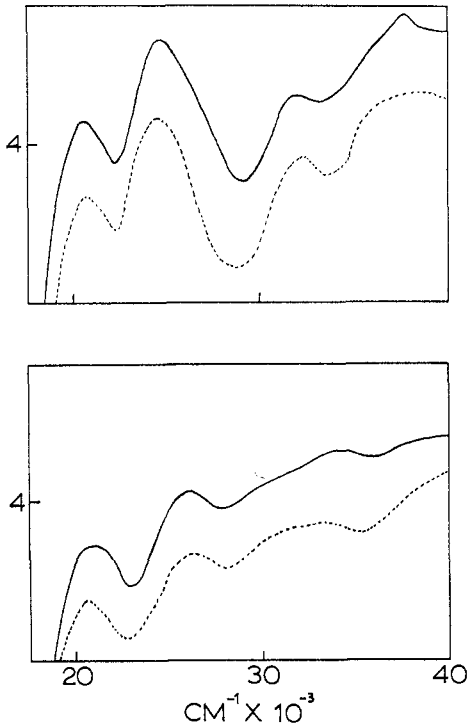


Figure 4.—Comparison of the electronic spectra of the red-brown (top) and brown (bottom) isomers.

Acknowledgment.—Support for this research from the National Science Foundation is gratefully acknowledged.

---

(13) E. König, *Inorg. Chem.*, **2**, 1238 (1963).
(14) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 73 (1959).