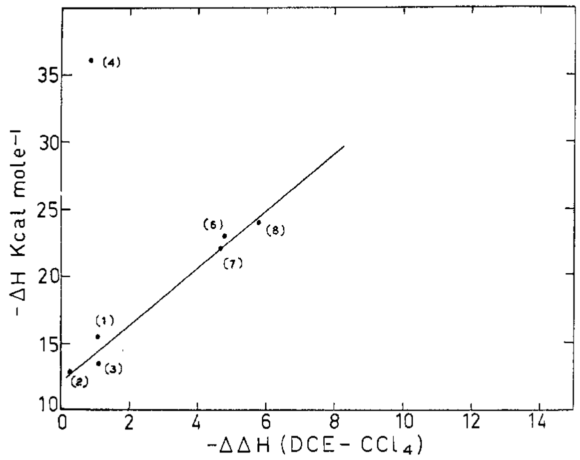

Figure 1.—Scatter in the $-\Delta H$ of the adduct formation *vs.* $-\Delta\Delta H$ of solvent transfer.

cases, the enthalpies for the formation of the diethyl ether, tetrahydrofuran, and pyridine adducts cause additional difficulties. The predicted enthalpies are 23.9, 28.9, and 41.8 compared to measured values of 19.2, 20.0, and 33.3. These differences are in the opposite direction of the expected solvent effect and may be due to the fact that steric effects outweigh any solvation effects. The larger discrepancy in the calculated and experimental heats for THF than for diethyl ether indicate that this is not the whole story and that complications from solvation are again present.

In addition to these complications, an additional problem was encountered with diethyl sulfide and the free radical base 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TMPN).[13] It was found that in $C_2H_4Cl_2$ the adducts ionize. TMPN gives a molar conductance of 24 ohm^{-1} mol^{-1} cm^2 at 1.2×10^{-3} *M* concentration at 25° and diethyl sulfide gives one of 23 ohm^{-1} mol^{-1} cm^2 at 2×10^{-3} *M* and 25°. The conductance of many 1:1 electrolytes is of the order of magnitude of 100 ohm^{-1} cm^2 mol^{-1} (± 25). The ionization process occurring in 1,2-dichloroethane could be attributed to the equilibrium

$$2SbCl_5\cdot B \rightleftharpoons SbCl_4(B)_2^+ + SbCl_6^-$$

Ionization is favored by a high dielectric constant solvent and a high donor strength (apparently large *C* number) of the base. Such an ionization process greatly complicates the interpretation of any heat measurement. The conductances of all of the other adducts reported here were minimal in 1,2-dichloroethane, but the results of similar measurements on many of the other systems reported in the literature[3] have not been published.

In conclusion and contrary to what we have been led to believe,[3] $SbCl_5$ investigated in the solvent 1,2-dichloroethane is a very poor reference acid for the quantitative determination of donor strength. Many of the applications in the literature of these donor number data are probably correct because these applications are very qualitative. Steric effects also influence the magnitude of the metal–ligand interaction in many of the transition metal ions to which these studies have been applied, so again such an effect would be in the same direction if the donor number were used, but we cannot expect the steric interaction in the transition metal ion complex to be quantitatively reproduced in $SbCl_5$. For all of the reasons described above, donor numbers clearly do not provide us with quantitative, fundamental information about the donor properties of bases. Complications arising from steric effects and the unusual solvating properties of 1,2-dichloroethane[12] give rise to significant and unpredictable contributions to the measured enthalpy. The *E* and *C* numbers reported here should enable us to predict enthalpies (in the absence of steric and appreciable solvent effects) to within 1 kcal mol^{-1}. As can be seen from Figure 1, we have not been able to find a reliable procedure that could be employed to correct the donor numbers for solvation effects.

Acknowledgment.—The authors acknowledge the generous support of the Paint Research Institute and the National Science Foundation, Grant No. 2554.

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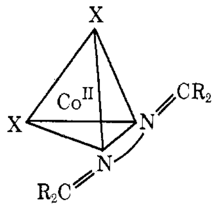
Complexes of Iron(II), Nickel(II), and Tin(IV) Chlorides with Hydrazine Derivatives[1]

By C. H. Stapfer,* R. W. D'Andrea, and R. H. Herber

Received May 14, 1971

The complexes of cobalt(II) halides with azines have been reported recently[2] wherein compounds of the type $R_2C{=}N{-}N{=}CR_2Co^{II}X_2$ were found to be tetrahedral complexes (I) which could be obtained by direct reaction of cobalt(II) halides with ketazines and aldazines or by condensation of bis hydrazine complexes of $Co^{II}X_2$ with ketones or aldehydes. The present work relates to the preparation of similar addition compounds of hydrazine derivatives with iron(II) and nickel(II) dichlorides as well as tin(IV) tetrachloride. The infrared and electronic spectra of the complexes of the transition metal halides were used to determine their probable structure, and resonance absorption of low energy γ radiation (Mössbauer effect) has proved to be a very useful tool for the tentative elucidation of the structure of the tin(IV) compounds.[3]



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(1) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., 1971, Abstract No. INOR-151.

(2) C. H. Stapfer and R. W. D'Andrea, *Inorg. Chem.*, **10**, 1224 (1971).

(3) For a general review of this field, see V. I. Gol'danski and R. H. Herber, "Chemical Applications of Mössbauer Spectroscopy," Academic Press, New York, N. Y., 1968.

Experimental Section

Magnetic suceptibility was measured by the Faraday method, the electronic spectra of the solid complexes were recorded on a Perkin-Elmer EPS 3T spectrophotometer, and the infrared spectra were obtained from potassium bromide wafers on a Perkin-Elmer 337 grating spectrometer. The experimental details of the Mössbauer technique have been discussed earlier.[2,4] All ^{119}Sn isomer shifts reported in the present paper are with respect to the centroid of a room-temperature $BaSnO_3$ spectrum. Velocity calibration was effected using a Pd (^{57}Co) source at room temperature in conjunction with a standard 0.8-mil, 99.99% pure iron foil (NBS SRM 1541) and the calibration data of Spijkerman, *et al.*[5] Spectra were accumulated so that at least 10^6 counts per channel were recorded. Since the resonance effect magnitude observed in these experiments was $\gtrsim 4\%$, the minimum signal to noise ratio was $\gtrsim 40$. Data reduction was effected by standard computational techniques.[5]

(Cyclohexanone azino)iron(II) Chloride.—Cyclohexanone (21 g, 0.2 mol) was added to a suspension of 10 g (0.05 mol) of the bis hydrazine complex of iron(II) chloride[6] in 50 ml of hexane and the reaction mixture was refluxed for 3 hr under nitrogen. Upon cooling, the resulting precipitate was filtered under nitrogen atmosphere, washed with hexane, and vacuum dried. The 15.7 g of an off-white amorphous solid represented a quantitative yield of (cyclohexanone azino)iron(II) chloride, sensitive to air and melting at 240° with decomposition. *Anal.* Calcd for $C_{12}H_{20}N_2Cl_2Fe$: C, 45.17; H, 6.30; N, 8.77; Cl, 22.22; Fe, 17.49. Found: C, 45.30; H, 5.93; N, 8.80; Cl, 22.09; Fe, 17.60. Infrared, cm^{-1}: 2920 (vs), 1590 (vs), 1470 (s), 1400 (m), 1300 (w), 1230 (w), 985 (w), 860 (w). Mol wt (by melting point depression in β-naphthol): calcd; 319; found, 340.

[(2,2′-Bipyridino)(cyclohexanone azino)]iron(II) Chloride.—A solution of 4.7 g (0.3 mol) of 2,2′-bipyridine in 50 ml of ethyl alcohol was added, at room temperature, to a solution of 1.2 g (0.1 mol) of anhydrous iron(II) chloride in 50 ml of ethyl alcohol.[7] The reaction mixture was maintained at 60° for 30 min under agitation and 1.9 g (0.1 mol) of cyclohexanone azine was added dropwise. After another 30 min of agitation at 60°, the solution was cooled in an ice bath and the crystallizing reaction product was filtered, washed with hexane, and recrystallized from ethyl alcohol to yield 4.5 g (70% theoretical) of [(2,2′-bipyridino)-(cyclohexanone azino)]iron(II) chloride in the form of deep red needles melting at 275° with decomposition. *Anal.* Calcd for $C_{22}H_{28}N_4Cl_2Fe$: C, 55.62; H, 5.93; N, 11.78; Cl, 14.92; Fe, 11.74. Found: C, 56.01; H, 5.60; N, 11.63; Cl, 14.88; Fe, 11.92. Mol wt: calcd, 475, found, 459.

(Cyclohexanone hydrazono)nickel(II) Chloride.—A suspension of 13 g (0.1 mol) of anhydrous nickel chloride in 500 ml of ethyl alcohol was refluxed until complete dissolution. To this solution was added 19.2 g (0.1 mol) of cyclohexanone azine and 1.8 g (0.1 mol) of water, and the reaction mixture was kept at reflux for 3 hr. Upon cooling, the resulting precipitate was filtered, washed with ethyl alcohol, and vacuum dried. The resulting 18.8 g of a pale green infusible solid represented a 78% yield of (cyclohexanone hydrazono)nickel(II) chloride. Evaporation of the mother liquor yielded 8 g of cyclohexanone. *Anal.* Calcd for $C_6H_{12}N_2Cl_2Ni$: C, 29.78; H, 5.00; N, 11.58; Cl, 29.33; Ni, 24.28. Found: C, 28.93; H, 4.93; N, 11.21; Cl, 30.00; Ni, 24.77. Infrared, cm^{-1}: 3250 vs, 2900 s, 1565 vs, 1440 m, 1290 m, 1235 w, 1170 vs, 970 m, 950 m, 585 vs, 500 w.

(Cyclohexanone azino)tin(IV) Chloride.—A solution of 2.6 g (0.1 mol) of anhydrous stannic chloride in 50 ml of *n*-hexane was added dropwise, at room temperature and under nitrogen atmosphere, to a solution of 1.92 g (0.1 mol) of cyclohexanone azine in 50 ml of *n*-hexane.

A fine white precipitate formed instantly and was filtered, washed with hexane, and then dried in the absence of air. The resulting 4.5 g of a white amorphous powder represented a quantitative yield of (cyclohexanone azino)tin(IV) chloride decomposing at room temperature upon extensive exposure to air. *Anal.* Calcd for $C_{12}H_{20}N_2Cl_4Sn$: C, 31.82; H, 4.45; N, 6.18; Cl, 31.23; Sn, 26.21. Found: C, 32.03; H, 4.30; N, 6.09; Cl, 32.00; Sn, 25.56. Infrared, cm^{-1}: 2910 (vs), 1650 (vs), 1430 (vs), 1345 (m), 1310 (m), 1240 (w), 985 (w), 900 (w). Mol wt: calcd, 451; found, 470.

Bis(benzalhydrazono)tin(IV) Chloride.—According to the general procedure outlined above, 2.6 g (0.1 mol) of anhydrous stannic chloride was dissolved in 50 ml of *n*-hexane and to this solution was slowly added 2.4 g (0.2 mol) of benzalhydrazone. The 36.5 g of an off-white amorphous solid obtained upon filtration represented a 73% yield of bis(benzalhydrazono)tin(IV) chloride melting at 110° with decomposition. *Anal.* Calcd for $C_{14}H_{16}N_4Cl_4Sn$: C, 33.57; H, 3.22; N, 11.18; Cl, 28.32; Sn, 23.70. Found: C, 33.44; H, 3.51; N, 10.97; Cl, 28.01; Sn, 24.02. Infrared, cm^{-1}: 3000 (s), 1615 (s), 1585 (s), 1560 (s), 1480 (w), 1440 (m), 1300 (m), 1270 (m), 1200 (m), 1075 (s), 940 (s), 850 (w), 740 (vs), 670 (vs), 495 (s).

Bis(hydrazino)tin(IV) Chloride.—In order to ensure the successful preparation of this compound, it is necessary to use strictly anhydrous hydrazine, which can easily be prepared from hydrazine sulfate and liquid ammonia.[8] In a modular drybox, under nitrogen atmosphere, a solution of 2.6 g (0.1 mol) of anhydrous stannic chloride in 50 ml of *n*-hexane was added dropwise to the heterogeneous mixture of 6.4 g (0.2 mol) of anhydrous hydrazine in 50 ml of *n*-hexane. A white precipitate formed immediately, which, after agitation at room temperature for 2 hr, was washed with hexane, filtered, and dried under vacuum in presence of P_2O_5. A quantitative amount of pure tin(IV) chloride dihydrazinate melting with decomposition at 70–80° was obtained. *Anal.* Calcd for $Sn^{IV}Cl_4(N_2H_4)_2$: H, 2.48; N, 17.26; Cl, 43.69; Sn, 36.56. Found: H, 2.55; N, 17.31; Cl, 43.83; Sn, 36.32. Infrared, cm^{-1}: 3400 m, 3100 vs, 1570 m, 1480 m, 1400 s, 1055 s, 925 s.

Results and Discussion

In contrast to cobalt(II) halides which form, at room temperature, brightly colored 1:1 complexes with azines,[2] iron(II) chloride, when allowed to react directly with these ligands between 20 and 100°, only yields uncharacterized viscous polymers. However, stable complexes of iron(II) chloride containing one ketazine ligand can easily be prepared by condensation of the bis-hydrazine complex of iron(II) chloride[6] with a ketone, one hydrazine being displaced in the process (eq 1). 2,2′-Bipyridine can also be displaced from

$$Fe^{II}Cl_2 + 2N_2H_4 \longrightarrow [(N_2H_4)_2Fe^{II}Cl_2] \xrightarrow{R_2C=O} [(R_2C=N-N=CR_2)Fe^{II}Cl_2] + N_2H_4 \qquad (1)$$

iron(II) by ketazines and the reaction of tris(2,2′-bipyridino)iron(II) chloride[7] with azines (AZ) at 60° leads to mixed bipyridino azine complexes in good yields (eq 2). The last bipyridine ligand, however,

$$Fe^{II}Cl_2 + \text{bipy} \xrightarrow{\text{EtOH}} [(\text{bipy})_3Fe^{II}Cl_2] \xrightarrow{\text{AZ}} [(\text{bipy})(\text{AZ})Fe^{II}Cl_2] + \text{bipy} \qquad (2)$$

cannot be dislodged to obtain the simple azine complexes of eq 1. The complexes of iron(II) chloride with ketazines are all soluble in *N*,*N*-dimethylformamide and conductometric titrations in that solvent indicate the formation of 2:1 electrolytes in which the two chlorides are replaced by the solvent. The reflectance spectra of azine complexes of the type $R_2C=N-N=CR_2$ are characteristic of tetrahedral iron(II) complexes. The sharp single absorption band observed at 4100 cm^{-1} is due to the $^5E \rightarrow {}^5T_2$ state transition and magnetic moments, at room temperature, of 4.9–5.0 BM, reflecting a small second order orbital contribution, are also consistent with a tetrahedral structure. In the infrared, the azine complexes of iron(II) chloride exhibit a characteristic N–N stretching absorption at 900 cm^{-1}

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(4) See for example R. H. Herber, S. C. Chandra, and Y. Hazony, *J. Chem. Phys.*, **53**, 3330 (1970), and references therein.

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which, according to prior observations, may be assigned to the bidentate character of the complexes. Several authors have reported the different N–N stretching vibrations of metal halide complexes containing bidentate[2,9,10] and unidentate[11,12] hydrazine groups, and it has been found generally useful to attribute these vibrations to bidentate hydrazine complexes when they occur in the 960–990-cm^{-1} region and to unidentate derivatives when they lie between 950 and 960 cm^{-1}. Molecular weight measurements in β-naphthol indicate that these complexes can exist in a monomeric form wherein the azine acts most likely as a chelating ligand thus imparting to the iron complexes a structure similar to that of the cobalt complexes reported earlier.[1]

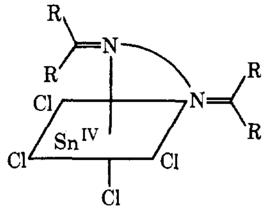
While neither cobalt(II) halides nor iron(II) chloride form stable complexes with hydrazones, we have observed that when nickel(II) chloride is allowed to react with cyclohexanone azine in the presence of water, cleavage of the azine occurs at one of the C=N bonds to form the green infusible (cyclohexanone hydrazono)-nickel(II) chloride (eq 3). On the other hand, nickel(II) chloride does not react directly with hydrazones nor does it form azinates when allowed to react with azines in the absence of water. The hydrazone complex of eq 3 is insoluble in all organic solvents except ketones and aldehydes with which it reacts and thus it appears to be highly polymeric. Its electronic spectrum exhibits several characteristic absorptions accountable for a tetrahedral structure. In the visible region a sharp absorption at 17,000 cm^{-1} can be assigned to the $T_1(F) \rightarrow T_1P$ transition and a shoulder near 20,000 cm^{-1} may be attributed to a charge-transfer absorption from the ultraviolet which may account for the green color of the complex. A somewhat weaker and broader absorption at 8200 cm^{-1} is assigned to the $T_1(F) \rightarrow A_2$ transition of the d^8 ion. In the infrared, a vibration at 970 cm^{-1} indicates the probable bidentate nature of the compound and a magnetic moment, at room temperature, of 3.6 BM accounts for the loss of degeneracy of the ground state in tetrahedral nickel complexes containing dissimilar ligands. Tin(IV) chloride reacts readily with both azines and hydrazones, under anhydrous conditions, to form metastable 1:1 complexes with azines and 2:1 adducts with hydrazones. The results of the resonant γ-ray absorption measurements on several of these reaction products, along with tin(IV) chloride dihydrazinate, are summarized in Table I. From the absence of resolvable quadrupole splitting of the resonance line in these compounds, it is inferred that the electric charge distribution around the metal atom has essentially cubic (octahedral) symmetry, despite the fact that two of the four nearest neighbor atoms are different from the remainder. Although all tetrahedral or octahedral organotin compounds of the type R_2SnL_2 (wherein R is alkyl or aryl and L is a ligand having at least one lone pair of electrons on the atom bonded to the metal) show a nonvanishing quadrupole interaction,[13,14] the absence of such an interaction in octahedral compounds of the type SnL_2X_4 (X = halogen) has been well documented in the literature[15-18] and the present results are consistent with such an octahedral configuration. The structure which emerges from these considerations is one in which the azine ligand functions as a bidentate moiety through the two nitrogen atoms, each of which has a lone pair of electrons available for bonding into the sp^{3}d^2 orbitals of the metal atom. This assumption is consistent with the zero quadrupole splitting and the presence in the infrared spectra of these compounds of a band at 985 cm^{-1} which is characteristic of the bidentate N–N vibrational mode. Since the ligand is too small to form a bonding of trans configuration on a single metal atom one may assume that such a trans complex would be polymeric. But the azine complexes of tin(IV) chloride are soluble in *N*,*N*-dimethylformamide in which they exist as undissociated monomers and a cis configuration (II) can reasonably be inferred. On the other hand, the bis hydrazine complex of tin(IV) chloride and bis(benzalhydrazono)tin(IV) chloride decompose in *N*,*N*-dimethylformamide, the latter yielding, upon cleavage of the hydrazone, benzaldazine and a mixture of tin(IV) chloride hydrazine and DMF adducts. Since, on the basis of steric considerations and electronegativity arguments, one might expect the lone pair nitrogen of the hydrazone to be more basic than the protonated nitrogen, it is reasonable to assume that bonding into the metal atom occurs with the unprotonated $-\ddot{N}=$ atom. The infrared spectra of the hydrazine and hydrazone complexes exhibit a strong absorption at 940 and 925 cm^{-1}, respectively, which may exclude a bridging bidentate structure. Thus, the hydrazone seems to act as a unidentate ligand to form an octahedral 2:1 complex (III). Steric considerations appear to favor the trans configuration although no definitive experimental evidence could be

$$R_2C{=}N{-}N{=}CR_2 + Ni^{II}Cl_2 \xrightarrow{H_2O} [(R_2C{=}N{-}NH_2)Ni^{II}Cl_2] + R_2C{=}O \qquad (3)$$

TABLE I
MÖSSBAUER PARAMETERS FOR COMPLEXES DISCUSSED IN THE TEXT[a]

Compound	T, °K	I.S.	Q.S.
$Sn^{IV}Cl_4(CH_3)_2C{=}N{-}N{=}C(CH_3)_2$	83	0.339	0
$Sn^{IV}Cl_4(C_5H_{10})C{=}N{-}N{=}C(C_5H_{10})$	85	0.334	0
$Sn^{IV}Cl_4(C_6H_5)CH{=}N{-}N{=}CH(C_6H_5)$	85	0.356	0
$Sn^{IV}Cl_4[(C_6H_5)CH{=}N{-}NH_2]_2$	83	0.301	0
$Sn^{IV}Cl_4(N_2H_4)_2$	94	0.316	0

[a] With respect to $BaSnO_3$.



II

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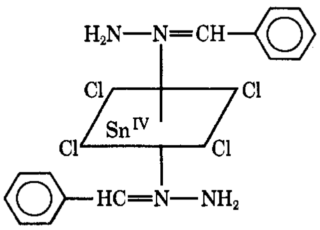

III

obtained from our infrared data. Finally, it should be noted that the similarity of the isomer shifts of the bis hydrazine complex of tin(IV) chloride and bis(benzalhydrazono)tin(IV) chloride does not necessarily imply that the metal–ligand interaction in the two cases is exactly identical.

Attempts to grow stable single crystals of the complexes discussed in this paper have thus far been unsuccessful but one X-ray investigation relating to the tris hydrazine hydrochloride complex of cobalt(II) chloride[2] is in progress.

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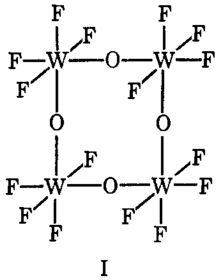
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

On the Structure and Bonding in the Tungsten Oxide Tetrafluoride Tetramer

BY M. J. BENNETT,* T. E. HAAS, AND J. T. PURDHAM

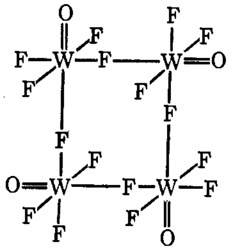
Received May 21, 1971

The solid-state structure of tungsten oxide tetrafluoride has been reported[1] as a tetrameric unit with idealized symmetry D_{4h} (I) and site symmetry C_{2h}.

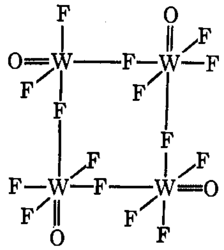


I

The assignment of the oxygen atoms to the bridging positions was based on the symmetry requirements of the space group and the stoichiometry of the compound. This assignment, which assumes an ordered structure, has been criticized[2] on the basis of the infrared and Raman spectra of $(WOF_4)_4$ in the solid state. In addition to the spectroscopic evidence we find that the observed bond lengths are inconsistent with an oxygen-bridged structure. All the data can be interpreted by a disorder of two orientations of an asymmetrically fluorine-bridged structure, II and III. The



II



III

idealized symmetry of the tetrameric unit is then C_{4h}. This disorder of oxygen and fluorine atoms is not without precedent in oxymetal fluoride systems;[3] *e.g.*, in the cesium salt of CrO_3F^-, the anion occupies a position with site symmetry S_4, and only one bond length (of 1.53 Å) is observed for the weighted average of Cr=O and Cr—F distances.

The relative merits of oxygen- and fluorine-bridged structures can be evaluated on the basis of expected bond lengths. A simple symmetry-based molecular orbital treatment of the oxygen-bridged structure shows that one might expect significant π bonding and hence a short tungsten–oxygen distance. The molecular orbitals, after construction of the σ framework, can be briefly described as follows for the D_{4h} oxygen-bridge model. Along each edge of the square array, perpendicular to the plane of the four metal atoms, a three-center W–O–W π-bonding system, consisting of dπ orbital from each metal and the corresponding oxygen pπ orbital, would result in bonding, nonbonding, and antibonding orbitals. Two electrons, those on the oxygen, are available to populate the bonding levels, thus giving an out-of-plane π-bond order of 0.5. In the plane a more extensively delocalized system results, but briefly the dπ orbitals transform as $A_{1g} + B_{2g} + E_u'$ and the oxygen pπ orbitals as $A_{1g} + B_{1g} + E_u$. The metal and oxygen A_{1g} and E_u orbitals give rise to bonding and antibonding combinations of each symmetry. The eight available electrons are housed in the A_{1g} and E_u bonding orbitals and the B_{1g} nonbonding orbital (which remains localized on the oxygen atoms). Thus a total in-plane π-bond order of 3 is distributed among the eight equivalent W–O linkages. The total $\sigma + \pi$ bond order is then 1.875 for each metal–oxygen bond. The approximate bond order *vs.* bond length curve of Cotton and Wing[4] would suggest a W–O bond of approximately 1.8 Å assuming that W–O distances parallel Mo–O distances. However the observed W–"O" distances are normal (2.10 and 2.12 Å) and correspond to an approximate bond order of 1.0.

Simple electron counting for a fluorine-bridged structure suggests one oxygen per tungsten atom and the pattern of in-plane and out-of-plane tungsten ligand distances[1] suggests that the oxygen atoms lie in the plane of the four tungsten atoms. These requirements allow three structures II, IV, and V. The particular arrangement and orientation of the tungsten atoms in this structure requires either or both of the diagonals to be coincident with symmetry elements, de-

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