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Molecular and Electronic Structure of a Novel Mixed-Valence Compound, μ-Oxo-decachloroditungstate(III,V)[1]

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The compound previously reported by Olsson as $K_2W(OH)Cl_5$ is shown to be the dimer $K_4[Cl_5WOWCl_5]$. The infrared spectra are consistent with C_{2v} molecular geometry resulting from a bent W–O–W bond with an angle $\phi \approx 140°$ and a force constant $k = 3.4$ mdyn/Å. Between 300 and 77°K, the temperature dependence of the magnetic moment indicates a magnetically isolated exchange-coupled dimer. The μ_{eff} data may be rationalized assuming spins $S_1 = S_2 = 1$, an exchange integral $J = -49$ cm^{-1}, and $g = 1.85$. An alternate assumption uses $S_1 = {}^3/_2$, $S_2 = {}^1/_2$, $J = -83$ cm^{-1}, and $g = 1.76$. The incomplete spin exchange provides independent evidence of a bent W–O–W bond. X-Ray investigations show that the compound is not isomorphous with $K_4[Cl_5ReOReCl_5]$ which has a linear Re–O–Re bond. In the electronic spectra, the intense band at 19,100 cm^{-1} ($\epsilon \sim$10,000 per W atom) is associated with two different oxidation states present. In agreement with evidence from the reduction of chlorotungstates and the disproportionation of the complex in solution, it is proposed that the compound should be considered as a W(III)–W(V) mixed-valence class II system.

Introduction

We have been studying for some time a deeply violet compound of tungsten[2] which forms in the course of reduction of chlorotungstates in hydrochloric acid solution. The intermediate which was isolated for the first time by Olsson[3] has been reported by him as well as by Collenberg and Backer[4] and thereafter[5-7] as $K_2W(OH)Cl_5$. However, our present results show clearly that the compound should be formulated correctly as the oxygen-bridged dimer $K_4[Cl_5WOWCl_5]$. In addition, we arrived at a comprehension of the molecular geometry and some insight into the electronic structure of the complex.

Recently, Colton and Rose[8] proposed the same general formula, although they were unable, on the basis of the assumed linear geometry, to account for the infrared frequencies of the W–O–W group. The purpose of this paper is, therefore, to furnish a reliable interpretation and a detailed discussion of the experimental data which may be used to characterize this unique compound.

Experimental Section

Preparation.—Potassium μ-oxo-decachloroditungstate was prepared according to the procedure of Olsson,[3] details having been reported previously.[2] The compound crystallizes in square platelets which are intensely red-violet in transmitted light and dark green in reflected light.

Instrumentation.—Infrared spectra were measured in Nujol mulls using Beckman IR-9 and IR-11 spectrometers. Frequencies are believed to be accurate to ±1 cm^{-1} for sharp bands. Preliminary investigations in the far-infrared region were effected by the reststrahlen method. Electronic spectra were obtained employing Cary 14 and Zeiss PMQ II/RA 2 spectrophotometers for measurements of absorption and reflectance spectra, respectively. Magnetic susceptibilities were determined by the Faraday method. The accuracy of measurement in terms of the magnetic moment is ±0.01 BM. X-Ray powder diffraction data were collected using a Norelco camera of diameter 114.6 mm and Cu Kα radiation. The density was determined by flotation to be 3.11 ± 0.02 g cm^{-3}.

Results and Discussion

Infrared Spectra.—The infrared spectra are characterized by bands at 652 (s), 374 (s, sharp), and 306 (vs) cm^{-1}, the 306-cm^{-1} band showing strong dissymmetry with individual bands centered at about 308 and 296 cm^{-1}. Following Hewkin and Griffith[9] (*cf.* also ref 8), the bands at 652 and 374 cm^{-1} may be assigned to the asymmetric and symmetric W–O–W stretches, ν_3 and ν_1, respectively. The deformation mode of the W–O–W bridge, ν_2, is expected to be outside the range covered by our measurements. The band at 306 cm^{-1} is due to the W–Cl stretch, its splitting being consistent with the C_{2v} symmetry of the compound (*vide infra*). In agreement with Colton and Rose,[8] we noticed that both the O–H stretching and the H–O–H bending modes are absent.

It is well known[9-11] that in case of *linear* oxygen-bridged transition metal complexes, the characteristic stretching modes of the bridge atoms are almost independent of the mass and type of the metal atom M involved, provided the mass of M is large compared to that of the bridge (*cf.* Table I). The frequencies ν_3 and ν_1 are then observed at about 850 and 220 cm^{-1}, respectively. Of the compounds listed in Table I, the first two were shown by X-ray crystal structure analysis to contain linear M–O–M groups;[12,13] for the remaining compounds this is very likely on the basis of their magnetic properties[14] and/or their infrared spectra.[9,10] For such linear systems, the symmetric stretching vibrations, ν_1, are forbidden in the infrared spectra. They

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[1] The experimental investigations were performed partly while the author was on a leave of absence at Mellon Institute, Pittsburgh, Pa.

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TABLE I

VIBRATIONAL FREQUENCIES AND FORCE CONSTANTS FOR LINEAR M–O–M GROUPS

		Obsd freq, cm^{-1}		Force const, mdyn/Å	
Compound	Ref	ν_3	ν_1	k	k_i
$K_4[Cl_5ReOReCl_5]$	9, 11	855	230	4.55	1.25
$K_4[Cl_5RuORuCl_5]$	9, 11	886	226	3.24	−0.19
$K_4[Br_5RuORuBr_5]$	9, 11	860	222	3.09	−0.14
$(NH_4)_4[Cl_5OsOOsCl_5]$	9, 11	848	...	...	...
$((CH_3)_4N)_4[Br_5OsOOsBr_5]$	9	846	...	...	...
$[(NH_3)_5CrOCr(NH_3)_5]Cl_4$	9	873	215	2.26	−0.85

may, however, be activated by crystal effects and, in fact, the bands observed at about 220 cm^{-1} are of rather weak intensity. The secular equation for linear M–O–M bridges may be written, in terms of the force constant k and the interaction constant k_i, as[15]

$$\begin{aligned}(5.889 \times 10^{-7})\nu_1^2 &= \frac{1}{m_M}(k + k_i)\\ (5.889 \times 10^{-7})\nu_3^2 &= \left[\frac{1}{m_M} + \frac{2}{m_O}\right](k - k_i)\end{aligned} \tag{1}$$

Here, m_i are the masses (amu) and ν_j are the frequencies (cm^{-1}). Cotton and Wing[10] calculated the values of k for the first four compounds in Table I to be between 3.73 and 3.48 mdyn/Å, assuming the then unknown ν_1 at 260 cm^{-1} and taking $k_i = 0.3$ mdyn/Å. The present knowledge of ν_1 fixes the values of k and k_i as shown in Table I. If eq 1 is applied to the tungsten compound considered here, $k = 17.06$ and $k_i = 6.61$ mdyn/Å are obtained. These values are not reasonable, since they would indicate a stronger metal–oxygen bond than in the compounds included in Table I, contrary to evidence from the magnetic behavior. The observed frequencies ν_1 and ν_3 are thus inconsistent with the assumption of a linear geometry for $K_4[Cl_5WOWCl_5]$.

Considering *bent* oxygen-bridged systems with the angle ϕ, the relevant secular equations are[10,15]

$$\begin{aligned}(5.889 \times 10^{-7})\nu_1^2 &= \left[\frac{1}{m_M} + \frac{1}{m_O}(1 + \cos\phi)\right](k + k_i)\\ (5.889 \times 10^{-7})\nu_3^2 &= \left[\frac{1}{m_M} + \frac{1}{m_O}(1 - \cos\phi)\right](k - k_i)\end{aligned} \tag{2}$$

Thus ν_3 is expected to have a frequency lower by a factor of about $[(1 - \cos\phi)/2]^{1/2}$ and ν_1 a frequency higher by about $[(1 + \cos\phi)(m_M/m_O)]^{1/2}$ than the linear system, if k and k_i remain fixed. In addition, the forbiddenness of ν_1 should be relaxed. This then is exactly what one observes for $K_4[Cl_5WOWCl_5]$. Since the masses of Re and W are very similar, we take $k_i = +1.25$ mdyn/Å over from the linear $K_4[Cl_5ReOReCl_5]$. Provided that this is a valid approximation and taking m_M as the mass of the tungsten atom, eq 2 yields $k = 3.37$ mdyn/Å and $\phi = 143° 20'$. Only slight changes are introduced if m_M is considered to represent the mass of the entire WCl_5 group (*viz.*, $k = 3.46$ mdyn/Å, $\phi = 139° 52'$). These values indicate a bent M–O–M bond which, in agreement with the magnetic properties, is weaker than in the corresponding linear rhenium compound.

Magnetic Properties.—The magnetic moments, μ_{eff}, which we determined vary between 2.40 BM at 293.5°K and 1.72 BM at 76.5°K per tungsten atom. In view of possible packing errors in applications of the Gouy method, the values are practically identical with those reported by Colton and Rose.[8] To compare with theory we assume at first that tungsten is present as tungsten(IV) and take the spin–orbit coupling constant as $\lambda = 1050$ cm^{-1}.[16] Then μ_{eff} of t_{2g}^2 is expected to vary, for the temperature range studied, between 1.10 and 0.80 BM in strict octahedral geometry,[17,18] between 2.30 and 2.00 BM for a large tetragonal distortion ($\Delta_{\text{axial}} = 10\lambda$),[19] and between slightly higher values for lower than axial symmetry.[16] The magnitude of μ_{eff} at room temperature is consistent with two unpaired electrons per tungsten atom. However, the pronounced decrease of the moment with decreasing temperature cannot be explained by normal spin–orbit, low-symmetry, and covalency effects on a cubic $^3T_{1g}$ ground term.

In the hexahalotungstates(IV), which have cubic K_2PtCl_6 structures, the observed low moment values are presumably due to antiferromagnetism *via* superexchange through intervening halogen atoms.[7] In $K_4[Cl_5WOWCl_5]$, *intra*molecular-exchange interaction is more likely to be present. The spin-coupling Hamiltonian may be written as

$$\mathcal{H} = -J\hat{S}_1 \cdot \hat{S}_2 \tag{3}$$

where J is the exchange integral and the $\hat{S}_i$'s are spin angular momentum operators. If constant terms in S_1 and S_2 are omitted, the eigenvalues of eq 3 are determined simply by

$$E = -{}^1/_2 JS(S + 1) \tag{4}$$

where $S = S_1 + S_2$. For a system of two unpaired spins on each metal atom, $S_1 = S_2 = 1$, and the energy values of eq 4 are 0(1), $-J$(3), and $-3J$(5), the degeneracy numbers being listed in parentheses. Application of the Van Vleck equation[20] readily yields the susceptibility per atom

$$\chi_A = \frac{Ng^2\beta^2}{kT}\left[\frac{\exp(-2x) + 5}{\exp(-3x) + 3\exp(-2x) + 5}\right] + N\alpha \tag{5}$$

Here, $x = J/kT$, g is the spectroscopic splitting factor, β is the Bohr magneton, and k is the Boltzmann constant. The temperature-independent paramagnetism $N\alpha$ is unlikely to be of importance for a $^3T_{1g}$ ground term[16] and is taken to be zero. With this assumption, we calculated χ_A as function of temperature for a large range of values of J and g. In Figure 1, curves of cal-

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culated $1/\chi_A$ are plotted for values of J and g marked thereon. Also included are, in terms of $1/\chi_A'$ values (where χ_A' is the susceptibility per tungsten atom corrected for the diamagnetism of the constituents[21]), the experimental results due to Colton and Rose.[8] It follows that the experimental susceptibilities may be adequately reproduced by assuming $J = -49$ cm^{-1} ($= -70k$) and $g = 1.85$.

From an investigation of the electronic spectra (*vide infra*) there is good reason to believe that $K_4[Cl_5WOWCl_5]$ may contain tungsten(III) and tungsten(V) in a 1:1 ratio. In this case, $S_1 = {}^3/_2$ and $S_2 = {}^1/_2$, the energies of eq 4 are $-J(3)$ and $-3J(5)$, and the susceptibility per atom is determined by

$$\chi_A = \frac{Ng^2\beta^2}{kT}\left[\frac{1 + 5\exp(2x)}{3 + 5\exp(2x)}\right] + N\alpha \qquad (6)$$

The best fit obtained on the assumption of $N\alpha = 0$ is included in Figure 1. It is characterized by $J = -83$ cm^{-1} ($= -120k$) and $g = 1.76$. In view of the possible margin of error, the approximation to the experimental $1/\chi_A'$ values is considered as adequate. Thus, on the basis of magnetic measurements *alone*, it is not possible to distinguish between the two cases discussed here.

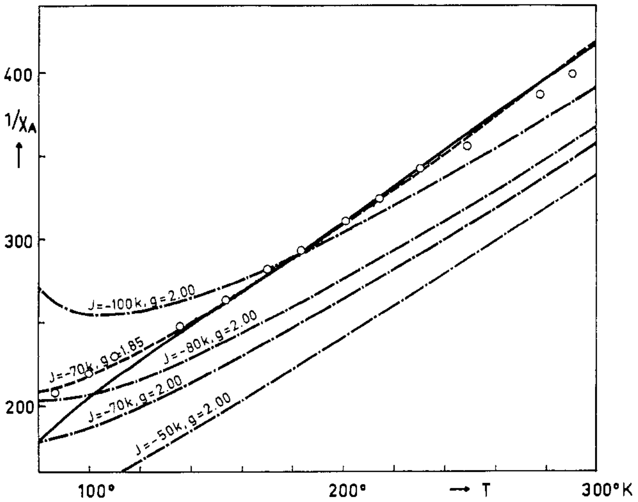

Figure 1.—Temperature dependence of ${}^1/\chi_A$ for $K_4[Cl_5WOWCl_5]$: broken curves, calculated according to eq 5 for values of J and g marked thereon; full curve, calculated according to eq 6 for $J = -120k$ and $g = 1.76$; ○, experimental values of $1/\chi_A'$.

However, it should be realized that, of the compounds listed in Table I, the first five are diamagnetic[9,22,23] and $[(NH_3)_5CrOCr(NH_3)_5]Cl_4$, although slightly paramagnetic at room temperature, assumes diamagnetism below 120°K.[24] In these linear oxygen-bridged systems, the spin exchange is thus complete. According to MO theory,[25-27] a linear W–O–W bridge with a total of eight valence electrons should also be diamagnetic. The observed moment of ~2.40 BM at 293.5°K is therefore further evidence of a nonlinear oxygen bridge in $K_4[Cl_5WOWCl_5]$.

X-Ray Diffraction.—The X-ray diffraction pattern of powdered $K_4[Cl_5WOWCl_5]$ was studied and the values of $\sin^2\theta$ were compared with those which were calculated for $K_4[Cl_5ReOReCl_5]\cdot H_2O$ on the basis of reported single-crystal data.[12] From the positions and the intensities of the lines, it is evident that the compounds are not isomorphous.

Electronic Spectra.—The electronic spectrum of $K_4[Cl_5WOWCl_5]$ between 10,000 and 47,000 cm^{-1} has been reported previously[2] and the most prominent features are compiled in Table II.

Table II

Electronic Spectrum of $K_4[Cl_5WOWCl_5]$

Wave-length, λ, mμ	Wave number, ν, cm^{-1}	Extinction coeff,[a] ε, M^{-1} cm^{-1}	Oscillator strength, f
(780)[b]	~12,800	<100	$<10^{-3}$
524	19,100	~10,000	1.2×10^{-1}
(436)?	~22,900	<200	$<10^{-3}$
390	25,600	<400	$\sim10^{-3}$
330	30,000	<400	$\sim10^{-3}$
254	39,400	>1000	$>10^{-2}$
228	43,900	>1000	$>10^{-2}$

[a] Per tungsten atom. [b] Numbers in parentheses indicate shoulders.

Assuming at first that the two tungsten atoms in $K_4[Cl_5WOWCl_5]$ may be considered as tungsten(IV), there are two transitions to be expected within the configuration 5d^2, *viz.*, ${}^3T_{1g}$ ($t_{2g}{}^2$) → ${}^3T_{2g}$ ($t_{2g}{}^1e_g{}^1$) and ${}^3T_{1g}$ ($t_{2g}{}^2$) → ${}^3T_{1g}$ ($t_{2g}{}^1e_g{}^1$), if the approximations of LS coupling and O_h symmetry are employed. In the $WCl_6{}^{2-}$ ion, the corresponding bands have been observed[28,29] at 19,230 and possibly at 31,750 cm^{-1} or at slightly lower wave number. Two weak bands are also encountered in $K_4[Cl_5WOWCl_5]$; their energies of 25,600 and 30,000 cm^{-1}, however, are not consistent with an assignment to d–d transitions in tungsten(IV). The intense bands in the ultraviolet region, which are observed in $K_4[Cl_5WOWCl_5]$ and likewise in the $WCl_6{}^{2-}$ and $WCl_6{}^-$ ions,[28,29] may be assigned to the $\pi(Cl) \rightarrow t_{2g}$ type of charge transfer.

The most peculiar characteristic of the spectrum of $K_4[Cl_5WOWCl_5]$ is a very intense band at 19,100 cm^{-1} (ϵ ~20,000); *cf.* Table II. Such extremely strong absorption in the visible region of the spectrum is indicated already by the dark green of the polycrystalline compound as distinguished from the red-violet of transmitted light of thin-crystal sections. The unusual nature of the band may be demonstrated by comparison

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with related oxygen-bridged compounds. Thus the electronic spectra of the $Cl_5ReOReCl_5^{4-}$ and $Cl_5RuORuCl_5^{4-}$ ions[30,31] do not show any intense bands below 28,000 and 26,000 cm^{-1}, respectively. Also, in the $(NH_3)_5CrOCr(NH_3)_5^{4+}$ ion, the bands[32,33] at 25,500 cm^{-1} ($\epsilon \sim 550$) and 30,000 cm^{-1} ($\epsilon \sim 650$) are much less intense than in the present case. In fact, it proves to be most difficult to find a reasonable assignment of the band as long as the compound is formulated as a ditungstate(IV). On the other hand, bands of comparable intensity in the visible region of the spectrum are often encountered in mixed-valence compounds.[34] Pertinent examples are the ruthenium red cation[35] $(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5^{6+}$ ($\epsilon \sim 21,000$ per Ru atom at 18,800 cm^{-1}) and presumably the incompletely characterized ion VOV^{4+} which forms in the reaction between vanadium(II) and vanadium(IV) in acid perchlorate solution ($\epsilon \sim 6800$ at 23,200 cm^{-1}).[36] These arguments demonstrate that, according to the classification due to Robin and Day,[34] the $Cl_5WOWCl_5^{4-}$ ion should be considered most likely as a W(III)–W(V) class II system. The high values of the extinction coefficient ϵ of the characteristic band and the exchange integral J suggest that some delocalization of valence electrons may take place and thus slight deviations from class II and toward class IIIa behavior are expected.

It has been pointed out[34] that, in favorable cases of class II compounds, the constituent ion absorptions may still be recognized, although the bands may not appear at exactly their normal frequencies. Indeed, the shoulder at about 12,800 cm^{-1} and the weak bands at 25,600 and 30,000 cm^{-1} (*cf.* Table II) could be associated with the spectrum of the $WOCl_5^{2-}$ ion which shows bands at 14,200, 25,190, and 32,790 cm^{-1}, respectively.[37] Unfortunately, no analogous complex ions of tungsten(III) having octahedral or tetragonal symmetry are known.

Disproportionation of the $Cl_5WOWCl_5^{4-}$ Ion and Reduction of Chlorotungstates in Solution.—We have shown previously,[2] on the basis of spectroscopic studies, that the $Cl_5WOWCl_5^{4-}$ ion is unstable in solution with respect to disproportionation into tungsten(III) and presumably tungsten(V) complex ions. The finding has given support to the suspicion that the parent ion, instead of containing tungsten(IV), might be a tungsten(III)–tungsten(V) compound. This result is substantiated by studies of the reduction of chlorotungstates in solution. Thus Lingane and Small[6] have demonstrated by polarographic methods that the coulometric reduction of chlorotungstates proceeds directly from tungsten(V) to tungsten(III). The strong hydrochloric acid solutions which are used to prepare $K_4[Cl_5WOWCl_5]$ contain presumably, after a one-electron reduction, tungsten(V) as the $WOCl_5^{2-}$ ion.[4,38] It is very likely that, after additional reduction, the $Cl_5WOWCl_5^{4-}$ ion forms in solution by direct reaction of $WOCl_5^{2-}$ and tungsten(III) complex ions. It may be concluded that both the formation and the disproportionation of the $Cl_5WOWCl_5^{4-}$ ion in solution are consistent with the formulation as a W(III)–W(V) mixed-valence compound.

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