One possible explanation for this might be that the assumption of only nearest-neighbor interaction is incorrect. In fact, in the analysis of the temperature dependence of the magnetic susceptibility of the simple complexes $M(hfac)_3(NITEt)_2$ (M = Gd, Eu) a fairly strong antiferromagnetic coupling between the radicals ought to be included,[39] and also the present europium chains show evidence of antiferromagnetic coupling between the radicals as large as 12 cm^{-1}. Therefore, it can be suspected that the large values of the parameters obtained from the fit of the magnetic susceptibility of $Gd(hfac)_3NITEt$ are actually artifacts, due to the neglect of the next-nearest-neighbor interactions. We are not aware of any kind of interaction that is suitable for our present compound; therefore, we tried to use a very simplified treatment in order to check the feasibility of the above hypothesis.

We simply reduced the chain to the contribution of two interpenetrating one-dimensional lattices, one formed by radicals and one by metal ions. We considered isotropic coupling within each lattice but not between lattices. In particular we used the Bonner–Fisher model[46] for $S = {}^1/_2$ antiferromagnetic Heisenberg chains and the Fisher expression[47] for classical Heisenberg chains with $S = {}^7/_2$. The experimental data could be fit reasonably well, given the roughness of the model, as shown in Figure 5. The values required for the fit need the antiferromagnetic coupling $J = 10.2$ cm^{-1} for the radicals and 0.28 cm^{-1} for the gadolinium ions. We do not attach any particular meaning to this fit, except that it gives some support to the hypothesis of next-nearest-neighbor coupling.

Registry No. $Eu(hfac)_3NITEt$, 117800-51-8; $Gd(hfac)_3NITEt$, 117800-52-9; $Eu(hfac)_3\cdot 2H_2O$, 20558-33-2; $Gd(hfac)_3\cdot 2H_2O$, 20558-32-1.

Supplementary Material Available: Table SI (complete crystallographic and experimental parameters), Table SII (distances and bond angles), and Table SIII (anisotropic thermal parameters) (10 pages); Table SIV (structure factors for $Gd(hfac)_3NITEt$) (25 pages). Ordering information is given on any current masthead page.

---

(46) Bonner, J. C.; Fisher, M. E. *Phys. Rev. A* **1964**, *135*, 640.
(47) Fisher, M. E. *Am. J. Phys.* **1964**, *32*, 343.

Contribution from Ames Laboratory,[1] USDOE, and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Vibrational and X-ray Photoelectron Spectroscopy for $MoWCl_4(PMe_3)_4$

Richard T. Carlin† and Robert E. McCarley*

Received April 19, 1988

Far-IR and Raman vibrational spectra and X-ray photoelectron spectra (XPS) have been obtained on the heteronuclear complex $MoWCl_4(PMe_3)_4$. A band at 326 cm^{-1} in the far-IR spectrum and at 322 cm^{-1} in the Raman spectrum has been attributed to the Mo–W stretching mode. The force constant for the heteronuclear M–M stretching mode is significantly larger compared to those of its homonuclear analogues. The XPS results for the heteronuclear complex indicate a partial shift in electron density from tungsten to molybdenum.

Introduction

Recently the structures and spectroscopic properties of the homologous series of quadruply bonded $M_2Cl_4(PMe_3)_4$ complexes, where $M_2 = Mo_2$, W_2, and MoW, have been reported in detail.[2] The structures indicate that the heteronuclear complex has M–M bonding characteristics intermediate between those of its homonuclear analogues. The M–M bond distances increase in the order Mo_2 (2.130 (0) Å)[3] < MoW (2.2092 (7) Å)[2] < W_2 (2.262 (1) Å).[3] The electronic spectra, electrochemical, and photoelectron results are consistent with this view.[2,4] We would like to report vibrational spectra and metal core-electron binding energies that provide additional information regarding this homologous series and that show apparent anomalous behavior for the heteronuclear complex.

Experimental Section

Materials. PMe_3 (Alfa Products) and $ClSiMe_3$ (Fisher Scientific Chemical Co.) were stored under vacuum and were freshly distilled under vacuum for each preparation. $BrSiMe_3$ (Aldrich Chemical Co.) was used as obtained. $Mo_2(O_2CCH_3)_4$,[5] $Mo_2(O_2CCMe_3)_4$,[5] $MoW(O_2CCMe_3)_4$,[6] and $W_2Cl_4(PMe_3)_4$[7] were synthesized according to literature procedures.

$MoWCl_4(PMe_3)_4$. The heteronuclear complex was prepared by a method developed in our laboratory.[8,9] $MoW(O_2CCMe_3)_4$ (0.45 g, 0.7 mmol) and excess PMe_3 (0.5 g, 5.0 mmol) were refluxed in ca. 15 mL of $ClSiMe_3$ for 2.5 days. After cooling, the mixture was filtered to give a green filtrate and a small quantity of a green solid. Excess $ClSiMe_3$ and PMe_3 were removed under vacuum leaving a blue-green, tarry residue. The green solid and filtrate were combined and were purified by heating under vacuum at 100 °C to expel any silyl ester resulting from reaction of $ClSiMe_3$ with the pivalate ligands. Subsequent extraction with cyclohexane yielded well-formed crystals. The heteronuclear complex was shown to be free of mononuclear impurities by ^{31}P NMR analysis.[2,8]

Table I. Far-IR Spectra of $Mo_2X_4(PR_3)_4$ Complexes[a]

complex	C–P–C bends		M–X str		ref
$Mo_2Cl_4(PMe_3)_4$	351 s	329 s	329 s	285 s	this work
$Mo_2Br_4(PMe_3)_4$	345 s	330 m	263 s	226 s	this work
$Mo_2Cl_4(PBu_3)_4$			326 m	278 m	11
$Mo_2Br_4(PBu_3)_4$			260 m		11
$Mo_2Cl_4(PEt_3)_4$			332 s	282 m	this work

assignments and wavenumbers, cm^{-1} (C–P–C bends, M–X str)

[a] Relative intensities are given as follows: s, strong; m, medium.

$Mo_2Cl_4(PMe_3)_4$. This homonuclear complex was prepared by using the same procedure as that used for the heteronuclear complex above except the homonuclear carboxylate $Mo_2(O_2CCMe_3)_4$ was used for the starting material.

$Mo_2Br_4(PMe_3)_4$. This complex was prepared from reaction of $Mo_2(O_2CCH_3)_4$ with $BrSiMe_3$ according to a described procedure using excess PMe_3.[9]

---

† Present address: Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 11201.

(1) Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences.
(2) Luck, R. L.; Morris, R. H.; Sawyer, J. F. *Inorg. Chem.* **1987**, *26*, 2422.
(3) Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040.
(4) Bancroft, G. M.; Bice, J.; Morris, R. H.; Luck, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 898.
(5) McCarley, R. E.; Templeton, J. L.; Colburn, T. J.; Katovic, V.; Hoxmeier, R. J. *Adv. Chem. Ser.* **1976**, *150*, 318.
(6) Katovic, V.; Templeton, J. L.; Homeier, R. J.; McCarley, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 5300.
(7) Sharp, P.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430.
(8) Carlin, R. T. Ph.D. Thesis, Iowa State University, 1982.
(9) Ryan, T. R.; McCarley, R. E. *Inorg. Chem.* **1982**, *21*, 2072.

0020-1669/89/1328-0280$01.50/0

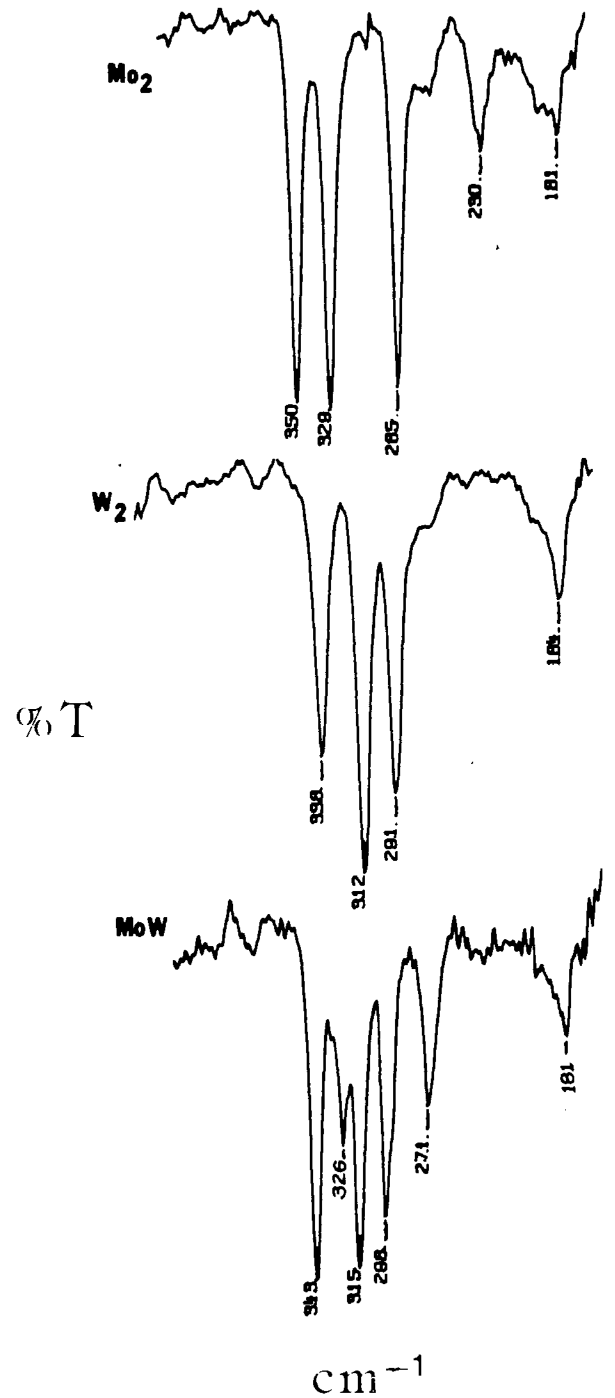

Figure 1. Far-IR spectra of $M_2Cl_4(PMe_3)_4$ complexes. Wavenumbers of absorption bands are given in cm^{-1}.

Physical Measurements. Far-IR spectra were obtained on an IBM IR/90 spectrometer using Nujol mulls on polyethylene disks. Raman spectra were obtained on an in-house instrument with excitation provided by an argon laser (514.5 nm). X-ray photoelectron (XPS) spectra were measured with an AEI-200B instrument using Al Kα radiation (1486.6 eV).

Results and Discussion

Vibrational Spectra. The symmetry of the $M_2X_4P_4$ skeletons for the two homonuclear complexes is D_{2d}, whereas the symmetry of the heteronuclear complex is C_{2v}. In D_{2d} symmetry, there are four M–Cl normal stretching modes of symmetries $A_1 + B_2 + E$. The stretching modes of B_2 and E symmetries are expected to be IR and Raman active, and the one of A_1 symmetry should be only Raman active. The M–M stretching mode, which is also of A_1 symmetry, should be only Raman active. Lowering the symmetry to C_{2v} for the heteronuclear complex causes the symmetries of the M–Cl stretching modes to become $2A_1 + B_1 + B_2$. All of these modes will be both IR and Raman active. Also, the M–M stretching mode in the heteronuclear dimer is of A_1 symmetry and is both IR and Raman active.

Table II. Far-IR Spectra of $M_2Cl_4(PMe_3)_4$ Complexes[a]

M_2	assignments and wavenumbers, cm^{-1}						
	C–P–C bend		M–X str		M–Cl bend or M–P str		M–M str
Mo_2	351 s	329 s	329 s	285 s	230 m	181 m	
W_2	338 s	312 s	312 s	291 s		184 m	
MoW	343 s	315 s	315 s	298 s		181 m	326 m

[a] Relative intensities are given as follows: s, strong; m, medium.

The far-IR spectra of the three $M_2Cl_4(PMe_3)_4$ complexes are shown in Figure 1. Assignment of the bands is aided by examination of the far-IR spectra of related dimolybdenum complexes summarized in Table I. The spectra of the trimethylphosphine-containing complexes are complicated by the presence of two bands arising from C–P–C bending modes of symmetries A_1 and E in the same spectral region as the M–Cl stretching modes. The tributylphosphine and triethylphosphine complexes do not exhibit these bending modes in the spectral region of interest.[10] Two M–Cl stretching bands are seen for $Mo_2Cl_4(PEt_3)_4$ and $Mo_2Cl_4(PBu_3)_1$ as expected from the D_{2d} symmetry of the molecules.[11] The spectrum of $Mo_2Cl_4(PMe_3)_4$ exhibits three bands in this same region, although four bands are expected: two M–Cl stretches and two C–P–C bends. By comparison with wavenumbers of the M–Cl stretching modes in the other dimolybdenum complexes, the bands at 329 and 285 cm^{-1} are assigned to M–Cl stretches. Upon replacement of Cl with Br, the band at 285 cm^{-1} is shifted to 226 cm^{-1}; however, the band at 329 cm^{-1} is only reduced in intensity, and a new band appears at 263 cm^{-1}. These shifts in the metal–halide stretching wavenumbers (ν(M–Br) $\approx$ 0.8 ν(M–Cl)) are the same as those observed for the tributylphosphine dimers, from 326 to 260 cm^{-1}. The reduction in the intensity of the band at 329 cm^{-1} upon replacement of Cl with Br indicates this band in the Cl complex is a result of two accidentally superposed fundamentals, one composed of a M–Cl stretching mode and the other composed of a C–P–C bending mode. In the bromide complex, this band, which appears at 330 cm^{-1}, is of only C–P–C bending character.

On the basis of the assignments discussed above, the various bands in the $M_2Cl_4(PMe_3)_4$ homologous series are listed in Table II along with their assignments. For all these complexes, the low-energy C–P–C bending-mode band is also assigned as the high-energy M–Cl stretching-mode band. The bands below 240 cm^{-1} have been tentatively assigned to M–Cl bending or M–P stretching modes. In the region composed of M–Cl stretching and C–P–C bending modes, the spectra are similar for the three complexes except that the heteronuclear dimer possesses two additional bands. These bands occur at 326 and 271 cm^{-1} and are assigned to the M–M stretching mode and the M–Cl stretching mode, both of A_1 symmetry. Similar bands are not observed for the homonuclear complexes because they are symmetry forbidden as discussed above. The assignment of the band at 271 cm^{-1} is based on the recently reported work of Gray and co-workers in which a band observed in the resonance Raman spectrum of $Mo_2Cl_4(PMe_3)_4$ at 274 cm^{-1} is assigned to the M–Cl stretching mode of A_1 symmetry.[12] Additionally, the Raman spectrum of $MoWCl_4(PMe_3)_4$ obtained in this work shows bands at 322 and 267 cm^{-1} corresponding to these same two infrared bands. The occurrence of these bands in the IR and Raman spectra of the heteronuclear complex and their absence in the IR of the ho-

---

(10) Maslowsky, E., Jr. *Vibrational Spectra of Organometallic Compounds*: John Wiley and Sons, Inc.: New York, 1977; p 8.

(11) San Filippo, J.; Sniadoch, H. J.; Grayson, R. L. *Inorg. Chem.* **1974**, *13*, 2121.

(12) Hopkins, M. D.; Schaefer, W. P.; Bronikowski, M. J.; Woodruff, W. H.; Miskowski, V. M.; Dallinger, R. F.; Gray, H. B. *J. Am. Chem. Soc.* **1987**, *109*, 408.

Table III. Wavenumbers[a] (ν) and Relative Force Constants (k) for M–M Stretching Modes from Raman Spectra

complex	ν, cm^{-1}	k, mdyn/Å	ref
$MoWCl_4(PMe_3)_4$	322 (3)	3.84	this work
$Mo_2Cl_4(PMe_3)_4$	354 (6)	3.54	this work
$Mo_2Cl_4(PBu_3)_4$	350 (1)	3.46	13
$W_2Cl_4(PBu_3)_4$	260 (10)	3.65	7
$Cr_2(mhp)_4$	556 (3)	4.73	13
$CrMo(mhp)_4$	504 (3)	5.03	13
$Mo_2(mhp)_4$	425 (3)	5.10	13
$MoW(mhp)_4$	384 (3)	5.45	13
$W_2(mhp)_4$	284 (3)	4.71	13

[a] Spectral resolution given in parentheses.

monuclear complexes is consistent with the assignments given here.

The M–M stretching frequencies obtained from Raman spectra for a number of $M_2Cl_4(PR_3)_4$ complexes as well as for $M_2(mhp)_4$ (mhp[5] = anion of 2-hydroxy-6-methylpyridine) complexes[13] are summarized in Table III. The relative force constants are calculated by using a simple harmonic oscillation approximation based on the metal atoms and ignores ligand contributions to the force constants. The Mo–W force constant for both homologous series, $M_2Cl_4(PMe_3)_4$ and $M_2(mhp)_4$, are anomalously greater than their homonuclear counterparts. It has been discussed, however, that this simple approach to the calculation of force constants should be viewed with caution.[12]

Another feature of the Raman spectrum of $MoWCl_4(PMe_3)_4$ worthy of note is that the intensity of the M–M stretch at 322 cm^{-1} is considerably less than that seen for $Mo_2Cl_4(PMe_3)_4$. A similar effect has been observed for pentachlorobis(2,5-dithiahexane)dirhenium, which possesses an asymmetric arrangement of ligands.[14] The M–M stretching mode for this dirhenium complex is seen in both the IR and Raman spectra; however, the Raman intensity is less than the intensities of other dirhenium complexes having M–M stretching modes with only Raman activity.[14]

X-ray Photoelectron Spectra. The results of X-ray photoelectron spectra (XPS) are summarized in Table IV. Binding energies are referenced to the C 1s binding energy taken as 285.0 eV. The chlorine $2p_{3/2}$ and the phosphorus 2s binding energies are essentially identical throughout the series. The Mo $3d_{5/2}$ binding energy in the MoW complex is 0.5 eV less than the Mo $3d_{5/2}$ binding energy in the Mo_2 complex. This is indicative of a lower effective charge (less positive charge) on Mo in the heteronuclear complex than in the homonuclear dimer. Surprisingly, a corresponding increase in the W $4f_{7/2}$ binding energy, expected by transfer of charge from W to Mo, was not observed. We believe however that the observed binding energies are correct, since the Cl $2p_{3/2}$ and P 2s binding energies for the MoW complex are consistent with those of the Mo_2 and W_2 complexes. Although the comparison of the binding energy changes on Mo and W are complicated by ionization from different orbital types, Mo $3d_{5/2}$ vs W $4f_{7/2}$, we still do not understand the lack of any change in the latter binding energy.

Table IV. Core-Electron Binding Energies (eV) for $M_2Cl_4(PMe_3)_4$ Determined from XPS[a]

	binding energy (±0.1 eV)			
complex	Mo $3d_{5/2}$	W $4f_{7/2}$	Cl $2p_{3/2}$	P 2s
Mo_2	229.2 (1.7/3.1)		198.7 (1.6/1.6)	131.6 (1.9)
MoW	228.7 (1.7/3.2)	32.2 (1.8/2.1)	198.7 (1.6/1.6)	131.5 (1.9)
W_2		32.2 (1.7/2.1)	198.7 (1.6/1.6)	131.5 (2.0)

[a] Fwhm (eV) for all orbitals and spin–orbit splittings (eV) for p, d, and f orbitals are given in parentheses as (FWHM/SOS).

Nonetheless, the shift of charge from W to Mo, indicated by the lowered binding energy of Mo, is consistent with the behavior of the ^{31}P NMR chemical shifts. For the two homonuclear dimers, the phosphine ligands are equivalent in each complex and are found at approximately the same chemical shift (δ(P–Mo) = –8.3 ppm for $Mo_2Cl_4(PMe_3)_4$ and δ(P–W) = –7.3 ppm for $W_2Cl_4(PMe_3)_4$). In the heteronuclear dimer the phosphine ligands on Mo are shifted upfield (shielded) to –27.9 ppm, and the phosphine ligands on W are shifted downfield (deshielded) to +11.2 ppm.[2,8]

Finally, the tendency for W to favor a higher oxidation state than Mo is shown by the reaction of $MoW(O_2CCMe_3)_4$ with I_2 to produce $MoW(O_2CCMe_3)_4I$.[6] The iodo ligand is found terminally bound to the W, giving W a formal oxidation state of +3, whereas the Mo remains in its +2 formal oxidation state.[6]

It may be that certain anomalous properties observed for the heteronuclear complexes arise from contribution of an ionic resonance configuration of the form $Mo^{\delta-}$–$W^{\delta+}$. Such ionic resonance stabilization has been put forward to explain greater bond energies between atoms of differing electronegativities versus their homonuclear analogues.[15]

---

(13) Bursten, B. E.; Cotton, F. A.; Cowley, A. H.; Hanson, B. E.; Lattman, M.; Stanley, G. G. *J. Am. Chem. Soc.* **1979**, *101*, 6244.

(14) San Filippo, J.; Sniadoch, H. J. *Inorg. Chem.* **1973**, *12*, 2326.

(15) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*: Haper & Row: New York, 1972; p 155.