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Preparation, Structures, and Spectra of Tetrakis(6-fluoro-2-oxypyridine)dichromium, -dimolybdenum, and -ditungsten: A Series of Polar Quadruple Bonds

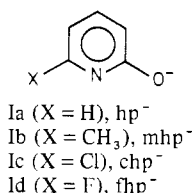
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By reactions in tetrahydrofuran of the lithium salt of 6-fluoro-2-hydroxypyridine, Li(fhp), with $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ or by reaction of Na(fhp) with a THF solution of WCl_4 , the three $\text{M}_2(\text{fhp})_4(\text{THF})$ compounds have been prepared. They have been characterized by X-ray crystallography and shown to have, in each case, a surprising, and unprecedented, molecular structure in which the four bridging fhp ligands are all oriented in the same direction. Thus, one metal atom in the molecule is coordinated entirely by nitrogen atoms and the other entirely by oxygen atoms. In addition, a THF molecule is axially coordinated to the latter metal atom. The molybdenum and tungsten compounds are crystallographically isomorphous, both crystallizing in space group $P2_12_12_1$ with $Z = 4$ and the following unit cell dimensions: for the Mo compound, $a = 16.446(3) \text{ \AA}$, $b = 17.290(2) \text{ \AA}$, $c = 9.166(2) \text{ \AA}$; for the W compound, $a = 16.497(3) \text{ \AA}$, $b = 17.315(4) \text{ \AA}$, $c = 9.176(2) \text{ \AA}$. The chromium compound crystallizes in space group Pn with $Z = 2$ and the following unit cell dimensions: $a = 11.684(2) \text{ \AA}$, $b = 9.243(1) \text{ \AA}$, $c = 13.958(3) \text{ \AA}$, $\beta = 90.90(3)^\circ$. In each case both enantiomorphs were refined and the one giving the lower residuals was used to calculate molecular dimensions. In the chromium compound the Cr-Cr distance, $2.150(2) \text{ \AA}$, is the only one in the range between $2.023(1)$ and $2.221(3) \text{ \AA}$ for a dichromium molecule with three-atom bridging ligands. The Mo-Mo and W-W distances, $2.092(1)$ and $2.185(2) \text{ \AA}$, are each somewhat longer than those previously found for substituted hydroxypyridine compounds, perhaps because of the axial THF ligands present. Some spectroscopic data are also given for the Mo and W compounds, as well as for the $\text{M}_2(\text{mhp})_4$ compounds, and assignments are proposed.

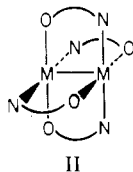
Introduction

The 2-oxypyridine type ligand I has played a prominent role

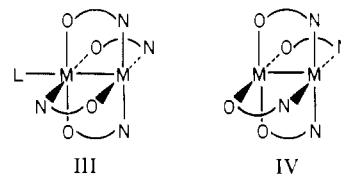


in the development of the chemistry of quadruply bonded dinuclear metal complexes.¹ It was with Ib, mhp $^-$, that the first complete series of stable group 6 M_2^{4+} complexes with a square-prismatic M_2X_6 central skeleton was obtained.² With ligands of this type a number of interesting phenomena have been examined, including (1) the behavior of strong Cr-Cr quadruple bonds,³⁻⁵ (2) the properties of heteronuclear (i.e., CrMo and MoW) compounds,⁶ (3) the chemical properties of W-W quadruple bonds,⁷ and (4) the systematic changes in photoelectron spectra through an entire vertical series of homologous compounds of group 6 molecules⁸ or through a horizontal series, viz., the Mo_2 , Ru_2 , and Pd_2 compounds.⁹

In general, these $\text{M}_2(\text{Xhp})_4$ molecules have structures in which two of the ligands are oriented in each direction to give a structure of the type illustrated schematically as II. For



several rhodium compounds in which there is axial coordination at one end only, an unsymmetrical ligand distribution of type III has been found.¹⁰ In no case, prior to this work, has the totally polar arrangement IV been observed.



The discovery of such compounds, which we report in this paper, was serendipitous; the work was begun with a different purpose. Following studies of group 6 compounds with the mhp ligand, Ib, we examined the properties of some homologous group 6 molecules containing either modified Xhp ligands or others closely related. We were especially interested in what effect such changes might have on the Cr-Cr bond length since $\text{Cr}_2(\text{mhp})_4$, with a bond length of $1.889(1) \text{ \AA}$,² was one of the early examples of a molecule with a "supershort" Cr-Cr quadruple bond. Bond lengths found for $\text{Cr}_2(\text{map})_4$, map = anion of 2-amino-6-methylpyridine, and $\text{Cr}_2(\text{dmhp})_4$, dmhp = 2,4-dimethyl-6-oxypyrimidine anion, were $1.870(3)$ ¹¹ and $1.907(3) \text{ \AA}$,¹² respectively, which do not differ from that in $\text{Cr}_2(\text{mhp})_4$ to any chemically significant extent. However, for $\text{Cr}_2(\text{chp})_4$, chp = 6-chloro-2-oxypyridine anion, Ic, the metal-metal distance was found¹³ to be $1.955(2) \text{ \AA}$, which is an increase of $0.006(3) \text{ \AA}$ from that of the analogous $\text{Cr}_2(\text{mhp})_4$. Prior to this, the entire range of Cr_2 compounds having this general type of ligand and lacking axial ligands was only $0.079(4) \text{ \AA}$, and for those compounds with type I ligands, only $0.034(8) \text{ \AA}$. The change in Cr-Cr bond length from $\text{Cr}_2(\text{mhp})_4$ to $\text{Cr}_2(\text{chp})_4$ is comparable to those caused by axial ligation,¹⁴ and yet it is the result of simply replacing the methyl group by Cl at the 6-position of the oxypyridine type ligand. We felt it was important to look for the cause of this bond-lengthening effect.

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Table I. Crystallographic Data for $M_2(\text{fhp})_4(\text{THF})$

formula	$\text{Cr}_2(\text{C}_5\text{H}_3\text{NOF})_4(\text{C}_4\text{H}_8\text{O}) \cdot (\text{C}_4\text{H}_8\text{O})$	$\text{Mo}_2(\text{C}_5\text{H}_3\text{NOF})_4(\text{C}_4\text{H}_8\text{O})$	$\text{W}_2(\text{C}_5\text{H}_3\text{NOF})_4(\text{C}_4\text{H}_8\text{O})$
fw	696.54	712.32	888.14
space group	Pn	$P2_12_12_1$	$P2_12_12_1$
a , Å	11.684 (2)	16.446 (3)	16.497 (3)
b , Å	9.243 (1)	17.290 (2)	17.315 (4)
c , Å	13.958 (3)	9.166 (2)	9.176 (2)
α , deg	90.0	90.0	90.0
β , deg	90.90 (3)	90.0	90.0
γ , deg	90.0	90.0	90.0
V , Å ³	1507.1 (8)	2606 (1)	2621 (1)
Z	2	4	4
d_{calcd} , g/cm ³	1.535	1.815	2.251
cryst size, mm	$0.5 \times 0.5 \times 0.4$	$0.5 \times 0.4 \times 0.4$	$0.4 \times 0.3 \times 0.3$
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	7.730	10.081	90.305
data colln instrument	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4	Syntex P1
radiation		Mo K α ($\lambda = 0.71073$ Å)	
scan method		$\theta-2\theta$	
data colln range (θ), deg	2.0–25.0	2.0–27.5	2.0–25.0
no. of unique data	2950	3359	2647
$F_o^2 \geq 3\sigma(F_o^2)$	1929	2678	1812
no. of parameters refined	350	352	352
R^a	0.065	0.030	0.046
R_w^b	0.080	0.039	0.054
quality-of-fit indicator ^c	2.2705	1.167	1.504
largest shift/esd, final cycle	0.45	0.15	0.03

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma(F_o)^2$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$.

Two hypotheses were entertained. According to one, the lone pairs on the Cl atom may donate some electron density into the Cr–Cr π^* orbital, thus weakening the bond. The other posits a dominant inductive effect, where replacement of a CH_3 group by the more electron-withdrawing Cl atom significantly weakens the ring nitrogen donor strength. The nitrogen atom would now behave more like an oxygen atom, and such a change would in principle be expected to increase the Cr–Cr bond length.

As a way of deciding between these two hypotheses, we planned to make the $\text{Cr}_2(\text{fhp})_4$ compound. Since the 6-fluorine atoms would have less of a donor interaction with the π^* orbitals of the Cr_2^{4+} moiety, the Cr–Cr bond in $\text{Cr}_2(\text{fhp})_4$ should be shorter than that in $\text{Cr}_2(\text{chp})_4$ if the first hypothesis is correct. On the other hand, since the fluorine atom is more electron withdrawing than the chlorine atom, the Cr–Cr bond should be longer in $\text{Cr}_2(\text{fhp})_4$ than in $\text{Cr}_2(\text{chp})_4$ if the second hypothesis is correct. With this reasoning in mind, we set out to make $\text{Cr}_2(\text{fhp})_4$, assuming that such a molecule, having the same qualitative structure as $\text{Cr}_2(\text{chp})_4$, would be easily prepared. Instead, we have obtained the unexpected result reported here, in which a ligand arrangement of type IV is observed, not only for the chromium compound but for the homologous molybdenum and tungsten compounds as well.

Experimental Section

Materials and Methods. All manipulations were carried out under an atmosphere of argon or nitrogen by using standard Schlenk techniques. The ligand 6-fluoro-2-hydroxypyridine (Hfhp) was obtained from Dow Chemical Co. $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$ were prepared according to established procedures.¹ All solvents used were dried over NaK alloy and distilled under nitrogen.

Preparation of $\text{Cr}_2(\text{fhp})_4(\text{THF}) \cdot \text{THF}$. In a typical reaction, 0.45 g (4 mmol) of 6-fluoro-2-hydroxypyridine was dissolved in 25 mL of THF. To this solution were added 2.5 mL of $n\text{-BuLi}$ (1.6 M in hexane) and then 0.17 g (0.5 mmol) of $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4$. The reaction mixture was allowed to stir overnight, resulting in a red solution along with solid LiO_2CCH_3 and undissolved product. This solution was filtered, concentrated to ca. 5 mL, and left undisturbed at -20°C . Large single crystals appeared in about 1 week in 75% yield.

Preparation of $\text{Mo}_2(\text{fhp})_4(\text{THF})$. A similar procedure was used for the molybdenum compound except that 0.43 g (1 mmol) of $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ was used. The reaction was stirred for 6 h and filtered. Crystals suitable for X-ray crystallography were obtained by layering the filtrate with an equal volume of hexane for slow diffusion. The

yield of crystalline product was 75%.

Preparation of $\text{W}_2(\text{fhp})_4(\text{THF})$. Sodium 6-fluoro-2-oxypyridinate (1.66 g, 12.28 mmol), prepared from Hfhp and NaOCH_3 in methanol, was dissolved in 100 mL of THF and the solution cooled to -25°C with an o -dichlorobenzene/ $\text{N}_2(\text{l})$ bath. To this was added 5.2 mL of 0.4% sodium amalgam (0.28 g of Na/5.2 mL of Hg). The mixture was stirred, and while it was still cold, 2.00 g (6.14 mmol) of WCl_4 was added. The reaction mixture was vigorously stirred and allowed to warm to room temperature slowly. After 4 h, 20 mL of the resulting deep red solution was filtered through Celite into a Schlenk tube. Very carefully, 20 mL of hexane was layered on top of this solution, and within 1 week the tube contained deep red, air-sensitive crystals in 50% yield.

X-ray Crystallography

$\text{Cr}_2(\text{fhp})_4(\text{THF}) \cdot \text{THF}$. A single crystal of dimensions $0.5 \times 0.5 \times 0.4$ mm was mounted with epoxy cement into a glass capillary. Unit cell constants were obtained and data collected on an Enraf-Nonius CAD-4 automated diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Lorentz and polarization corrections were applied.¹⁵ The systematic absence ($h0l$) $h + l = 2n + 1$, along with successful refinement, identified the correct space group as Pn .

The metal atom positions were determined from a Patterson map, and the remaining non-hydrogen atoms were obtained from alternating least-squares cycles and difference maps. Of 2950 unique data collected, those 1929 with $I > 3\sigma(I)$ were used to refine 350 variables to final discrepancy indices $R = 0.065$ and $R_w = 0.080$. Full crystallographic data for all three compounds as well as expressions for R , R_w , and w are given in Table I. Refinement of the enantiomorph gave slightly inferior results. The one peak in the final difference Fourier over $1.0 \text{ e}/\text{Å}^3$ (1.238) resides near the four fluorine atoms and is 1.850 Å from F(2) and 2.101 Å from F(1). We attribute no chemical significance to this peak. All five solvent atoms and the axial THF carbon atoms were left isotropic for an optimum data to parameter ratio.

$\text{Mo}_2(\text{fhp})_4(\text{THF})$. Data collection and reduction for this compound were similar to those for $\text{Cr}_2(\text{fhp})_4(\text{THF}) \cdot \text{THF}$. The cell parameters, volume, space group, and Patterson map were identical with those found in the previously determined $\text{W}_2(\text{fhp})_4(\text{THF})$ (next section), and refinement was commenced with the atomic positions of the tungsten compound. Full-matrix least-squares refinement of the 47 anisotropic, non-hydrogen atoms converged to final values of $R = 0.030$

(15) All crystallographic calculations were done on a PDP 11/60 computer employing the Enraf-Nonius Structure Determination Package at B. A. Frenz Associates, College Station, TX.

Table II. Final Positional Parameters for $\text{Cr}_2(\text{fhp})_4(\text{THF})\cdot\text{THF}$

atom	x	y	z	atom	x	y	z
Cr(1)	0.000	0.1495 (2)	0.000	C(8)	0.047 (1)	0.687 (1)	-0.116 (1)
Cr(2)	0.1649 (2)	0.2409 (2)	0.0337 (2)	C(9)	0.159 (1)	0.680 (1)	-0.077 (1)
F(1)	0.2758 (6)	0.4229 (9)	0.1984 (6)	C(10)	0.189 (1)	0.552 (1)	-0.0395 (9)
F(2)	0.2923 (6)	0.5292 (8)	0.0002 (6)	C(11)	0.158 (1)	0.074 (1)	-0.1483 (7)
F(3)	0.4001 (6)	0.2659 (9)	-0.0626 (6)	C(12)	0.198 (1)	0.007 (1)	-0.2320 (9)
F(4)	0.3854 (7)	0.1503 (9)	0.1394 (7)	C(13)	0.307 (1)	0.030 (2)	-0.2561 (9)
O	-0.1751 (7)	0.0554 (8)	-0.0337 (6)	C(14)	0.384 (1)	0.116 (2)	-0.204 (1)
O(1)	-0.0649 (7)	0.2268 (8)	0.1192 (5)	C(15)	0.338 (1)	0.181 (1)	-0.1207 (9)
O(2)	-0.0489 (7)	0.3271 (9)	-0.0695 (6)	C(16)	0.138 (1)	-0.053 (1)	-0.1076 (8)
O(3)	0.0556 (6)	0.0621 (8)	-0.1191 (5)	C(17)	0.164 (1)	-0.187 (1)	0.1591 (9)
O(4)	0.0399 (7)	-0.0346 (8)	0.0690 (6)	C(18)	0.271 (1)	-0.199 (1)	0.198 (1)
N(1)	0.1065 (8)	0.3261 (9)	0.1611 (6)	C(19)	0.357 (1)	-0.082 (2)	0.198 (1)
N(2)	0.1213 (8)	0.4316 (9)	-0.0329 (6)	C(20)	0.318 (1)	0.034 (1)	0.147 (1)
N(3)	0.2307 (7)	0.161 (1)	-0.0940 (6)	C(21)	-0.280 (1)	0.135 (2)	-0.022 (1)
N(4)	0.2152 (7)	0.0569 (9)	0.1046 (6)	C(22)	-0.370 (2)	0.014 (3)	-0.016 (2)
C(1)	-0.007 (1)	0.298 (1)	0.1799 (8)	C(23)	-0.331 (2)	-0.093 (2)	-0.091 (1)
C(2)	-0.053 (1)	0.357 (2)	0.2656 (9)	C(24)	-0.199 (1)	-0.087 (2)	-0.065 (1)
C(3)	0.006 (1)	0.438 (1)	0.327 (1)	O(s)	0.033 (3)	0.444 (4)	0.606 (2)
C(4)	0.128 (1)	0.469 (1)	0.3074 (9)	C(25)	0.131 (2)	0.522 (3)	0.549 (2)
C(5)	0.167 (1)	0.404 (1)	0.2228 (9)	C(26)	0.234 (2)	0.469 (3)	0.586 (2)
C(6)	0.0142 (9)	0.441 (1)	-0.0734 (8)	C(27)	0.204 (4)	0.415 (5)	0.688 (3)
C(7)	-0.024 (1)	0.575 (1)	-0.1132 (9)	C(28)	0.089 (2)	0.360 (3)	0.680 (2)

Table III. Final Positional Parameters for $\text{Mo}_2(\text{fhp})_4(\text{THF})$

atom	x	y	z	atom	x	y	z
Mo(1)	0.02375 (3)	0.12970 (3)	0.06240 (5)	C(6)	0.1468 (3)	0.1867 (3)	-0.1431 (6)
Mo(2)	0.09008 (3)	0.21638 (3)	0.16821 (5)	C(7)	0.1905 (4)	0.1957 (4)	-0.2752 (7)
F(1)	0.0834 (3)	0.2946 (2)	0.4781 (4)	C(8)	0.2526 (4)	0.2494 (4)	-0.2807 (7)
F(2)	0.2365 (2)	0.3245 (2)	0.0813 (4)	C(9)	0.2695 (3)	0.2950 (4)	-0.1608 (8)
F(3)	0.2468 (2)	0.2226 (2)	0.3646 (4)	C(10)	0.2231 (3)	0.2824 (3)	-0.0406 (7)
F(4)	0.0775 (3)	0.3981 (2)	0.2009 (5)	C(11)	0.1623 (4)	0.0559 (3)	0.2105 (6)
O	0.5609 (3)	0.9713 (3)	0.4332 (6)	C(12)	0.2157 (4)	-0.0028 (4)	0.2621 (8)
O(1)	-0.0521 (2)	0.1085 (2)	0.2399 (4)	C(13)	0.2793 (4)	0.0176 (5)	0.3476 (8)
O(2)	0.0885 (2)	0.1365 (2)	-0.1303 (4)	C(14)	0.2931 (4)	0.0925 (5)	0.3876 (8)
O(3)	0.0996 (2)	0.0410 (2)	0.1298 (5)	C(15)	0.2386 (3)	0.1447 (4)	0.3365 (7)
O(4)	-0.0608 (2)	0.2077 (2)	-0.0234 (4)	C(16)	-0.0549 (3)	0.2792 (3)	0.0019 (6)
N(1)	0.0159 (3)	0.2035 (3)	0.3625 (5)	C(17)	-0.1106 (4)	0.3322 (4)	-0.0564 (8)
N(2)	0.1639 (3)	0.2325 (2)	-0.0255 (5)	C(18)	-0.0995 (5)	0.4119 (4)	-0.0248 (8)
N(3)	0.1754 (3)	0.1313 (3)	0.2495 (5)	C(19)	-0.0356 (5)	0.4356 (4)	0.0650 (9)
N(4)	0.0077 (3)	0.3036 (3)	0.0897 (5)	C(20)	0.0152 (4)	0.3809 (3)	0.1144 (7)
C(1)	-0.0430 (3)	0.1462 (3)	0.3592 (6)	C(21)	0.6399 (5)	0.9914 (5)	0.472 (1)
C(2)	-0.0922 (4)	0.1315 (4)	0.4818 (7)	C(22)	0.6735 (6)	1.0408 (6)	0.358 (1)
C(3)	-0.0784 (4)	0.1776 (5)	0.6085 (7)	C(23)	0.6063 (6)	1.0579 (5)	0.254 (1)
C(4)	-0.0195 (5)	0.2364 (4)	0.6096 (7)	C(24)	0.5308 (6)	1.0218 (5)	0.324 (1)
C(5)	0.0239 (4)	0.2434 (4)	0.4841 (7)				

and $R_w = 0.039$. As with the chromium and tungsten compounds, refinement of the enantiomorph gave inferior results. The largest peak in the final difference map was $0.44 \text{ e}/\text{\AA}^3$.

$\text{W}_2(\text{fhp})_4(\text{THF})$. A single crystal ($0.4 \times 0.3 \times 0.3 \text{ mm}$) mounted in a glass capillary was placed on a Syntex P1 four-circle diffractometer equipped with graphite-monochromated Mo K α radiation. Data were collected in the orthorhombic system with systematic absences uniquely determining the space group as $P2_12_12_1$. Lorentz, polarization, and absorption corrections were applied.

The tungsten positions were calculated from the Patterson function, and successive least-squares cycles and difference Fourier maps revealed the positions of the remaining non-hydrogen atoms. Final discrepancy indices were $R = 0.046$ and $R_w = 0.054$. The largest peak in the final difference map was $0.58 \text{ e}/\text{\AA}^3$.

Spectroscopic Measurements

Infrared spectra ($600\text{--}300 \text{ cm}^{-1}$) were recorded with THF solutions of the compounds in CsI cells on a Perkin-Elmer 283B spectrophotometer. The Raman spectrum of solid $\text{Mo}_2(\text{fhp})_4(\text{THF})$ was recorded by using a rotating-wheel sample mount on a Cary Raman spectrometer, with a 4880-\AA exciting line. A Cary 17D spectrophotometer was used to obtain the UV-vis spectra at room temperature (THF solution) and at 5 K (KBr pellet). Numerical data for the spectral region we shall discuss are given in Table VII.

Results and Discussion

Structures. Final positional parameters for $\text{Cr}_2(\text{fhp})_4(\text{THF})\cdot\text{THF}$, $\text{Mo}_2(\text{fhp})_4(\text{THF})$, and $\text{W}_2(\text{fhp})_4(\text{THF})$ are given

in Tables II–IV, respectively. Table V gives selected bond distances and angles of the three $\text{M}_2(\text{fhp})_4(\text{THF})$ structures, and Table VI gives chemically averaged bond distances and angles. Figure 1 is an ORTEP plot of a representative $\text{M}_2(\text{fhp})_4(\text{THF})$ unit.

The three $\text{M}_2(\text{fhp})_4(\text{THF})$ molecules, where $M = \text{Cr}, \text{Mo},$ or W , each reside on general positions with one molecule in the asymmetric unit. The Mo and W compounds are isomorphous while the Cr analogue crystallizes differently and has an extra THF solvent molecule in the lattice. We now describe some notable features in the $\text{M}_2(\text{fhp})_4(\text{THF})$ structures.

The most striking feature of these compounds is the arrangement of the ligands around the dimer. The four bridging 6-fluoro-2-oxypyridine groups are all oriented in one direction along the metal–metal vector with the four fluorine atoms forming a square around one axial position. At the other axial position is a coordinated THF molecule. As noted in the introduction, such an arrangement is unprecedented. As expected, the axially coordinated oxygen atom of the THF molecule is closer to the metal in the chromium compound ($2.266(6) \text{ \AA}$) than in the molybdenum ($2.528(5) \text{ \AA}$) and tungsten ($2.49(2) \text{ \AA}$) compounds.

Of special interest in these structures is the metal-to-metal quadruple bond distance. For $\text{Cr}_2(\text{fhp})_4(\text{THF})\cdot\text{THF}$, the

Table IV. Final Positional Parameters for $W_2(\text{fhp})_4(\text{THF})$

atom	x	y	z	atom	x	y	z
W(1)	0.02290 (6)	0.12750 (6)	0.0587 (1)	C(6)	0.143 (1)	0.187 (1)	-0.143 (3)
W(2)	0.09151 (6)	0.21800 (6)	0.1698 (1)	C(7)	0.191 (2)	0.193 (1)	-0.272 (3)
F(1)	0.584 (1)	0.204 (1)	0.523 (2)	C(8)	0.251 (2)	0.251 (2)	-0.272 (3)
F(2)	0.764 (1)	0.8260 (9)	0.416 (2)	C(9)	0.269 (2)	0.299 (1)	-0.157 (3)
F(3)	0.247 (1)	0.221 (1)	0.366 (2)	C(10)	0.222 (2)	0.284 (1)	-0.039 (3)
F(4)	0.426 (1)	0.6037 (8)	0.704 (2)	C(11)	0.159 (1)	0.057 (1)	0.208 (3)
O	0.561 (1)	0.971 (1)	0.433 (3)	C(12)	0.215 (2)	-0.002 (2)	0.256 (3)
O(1)	0.5517 (9)	0.8933 (9)	0.737 (2)	C(13)	0.281 (2)	0.019 (2)	0.342 (3)
O(2)	0.4104 (9)	0.8632 (9)	0.372 (2)	C(14)	0.294 (2)	0.097 (2)	0.383 (3)
O(3)	0.100 (1)	0.0410 (9)	0.130 (2)	C(15)	0.239 (1)	0.144 (1)	0.330 (3)
O(4)	-0.060 (1)	0.2050 (9)	-0.023 (2)	C(16)	-0.054 (1)	0.280 (1)	-0.002 (2)
N(1)	0.016 (1)	0.201 (1)	0.360 (2)	C(17)	-0.109 (2)	0.335 (1)	-0.058 (3)
N(2)	0.165 (1)	0.234 (1)	-0.021 (2)	C(18)	-0.099 (2)	0.414 (2)	-0.033 (4)
N(3)	0.174 (1)	0.134 (1)	0.247 (2)	C(19)	-0.035 (2)	0.434 (1)	0.060 (4)
N(4)	0.007 (1)	0.306 (1)	0.088 (2)	C(20)	0.017 (2)	0.380 (1)	0.117 (3)
C(1)	-0.046 (2)	0.145 (1)	0.359 (2)	C(21)	-0.142 (2)	0.004 (2)	-0.033 (5)
C(2)	-0.094 (2)	0.130 (2)	0.476 (3)	C(22)	-0.175 (2)	-0.041 (3)	-0.144 (4)
C(3)	-0.080 (2)	0.170 (2)	0.600 (3)	C(23)	-0.109 (2)	-0.058 (2)	-0.251 (5)
C(4)	-0.016 (2)	0.232 (2)	0.605 (3)	C(24)	-0.035 (2)	-0.022 (2)	-0.201 (6)
C(5)	0.023 (2)	0.245 (2)	0.486 (3)				

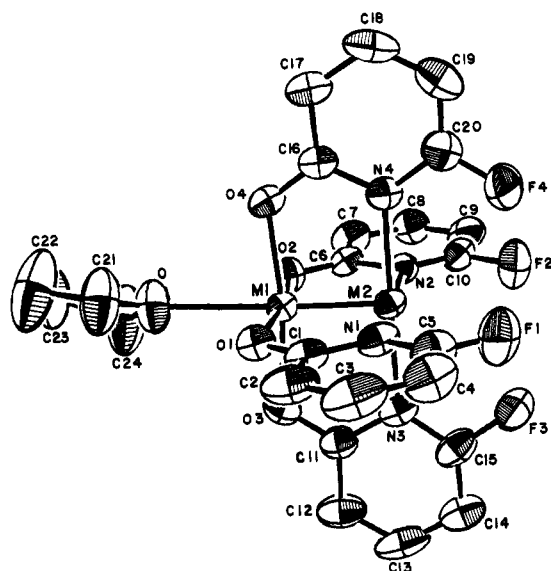


Figure 1. ORTEP drawing of the molecular unit found in all three compounds. The atom-labeling scheme shown applies to the Mo and W compounds. For the Cr compound, permute the ligands as follows: (1,2,3,4) \rightarrow (1,3,4,2), where the ligand numbers are the numbers assigned to their O, F, and N atoms.

Cr–Cr bond length is 2.150 (2) Å. This distance is unusual in the wide spectrum of Cr–Cr quadruple-bond lengths. It lies between the “supershort” $\text{Cr}^4\text{--Cr}$ bonds (<1.90 Å) and those of the dichromium tetracarboxylates (2.2–2.6 Å). The bond distance is closest to that seen in $\text{Cr}_2(\text{CH}_2\text{SiMe}_3)_4(\text{PMe}_3)_2$ (2.100 (1) Å)¹⁶ and seems to fall near metal–metal distances seen in organo dichromium compounds in general. We note that the Cr–Cr separation is longer than that in the Mo compound, 2.092 (1) Å, which further illustrates the extreme sensitivity of the Cr–Cr quadruply bonded systems to axial interaction.

The Mo–Mo distance is significantly greater than that reported for $\text{Mo}_2(\text{chp})_4$,¹⁴ 2.085 (1) Å, and related type compounds $\text{Mo}_2(\text{DMP})_4$,² 2.064 (1) Å, $\text{Mo}_2(\text{mhp})_4$,¹¹ 2.065 (1) Å, and $\text{Mo}_2(\text{map})_4$,¹² 2.070 (1) Å. The W–W distance, at 2.185 (2) Å, is significantly longer than the distances found in the $\text{W}_2(\text{mhp})_4$,¹¹ $\text{W}_2(\text{dmhp})_4$, $\text{W}_2(\text{map})_4$,¹² and $\text{W}_2(\text{chp})_4$,¹⁴ structures, which range from 2.155 (2) to 2.177 (1) Å. For both Mo and W compounds, the metal–metal distance is the

longest for the class of dimers bridged by N–C–O type ligands. These separations are now approaching the distances found in dimolybdenum and ditungsten tetrakis(carboxylato) compounds.

The metal–ligand distances and angles along with important ligand–ligand values are given in Table V. The remaining bond lengths and angles are typical of these systems and are available as supplementary material.

Finally, there is a question of the highest importance concerning these unprecedented structures, namely why they occur. Noting that for all three compounds the preparations are carried out in the coordinating solvent THF and that the products all have a molecule of THF coordinated to one metal atom, we might consider the possibility that coordinated THF participates at one or more crucial stages in the formation of the $M_2(\text{fhp})_4$ molecules and exercises a steric and/or electronic influence favoring the distribution of fhp ligands in which all of the more sterically congested nitrogen sides are directed to the other metal atom. This would imply that in the absence of THF (or other coordinating solvent) the more symmetrical ligand arrangement II would be obtained. Unfortunately, methods for preparing these compounds, especially the chromium and tungsten compounds, in noncoordinating solvents are not known, nor easy to envision.

If it is true that molecules with ligand arrangement II would be more stable than those with arrangement IV in the absence of potential axial ligands, the interesting question arises as to whether the THF could be removed and rearrangement from distribution IV to II could be thermally induced. We intend to investigate this point in the future.

Spectra. The visible spectra of the molybdenum and tungsten compounds in the region where the $\delta \rightarrow \delta^*$ transitions might be expected are shown in Figure 2. Additional spectral features are recorded in Table VII. In Figure 2 a compound peak is seen for $\text{W}_2(\text{fhp})_4$, and an approximate deconvolution of this envelope suggests that the lower energy absorption band is at about 20 000 cm^{-1} . This can probably be assigned to the $\delta \rightarrow \delta^*$ transition, while the stronger band at ca. 21 050 cm^{-1} is probably a charge-transfer band of the $\delta \rightarrow \pi_L^*$ type (where π_L^* designates a combination of antibonding π orbitals of the ligands). The appearance of the $\text{W}_2(\text{fhp})_4$ spectrum in this region is not very different from that of $\text{W}_2(\text{mhp})_4$, which has a similar band with a maximum at 19 400 cm^{-1} and a shoulder at ca. 18 600 cm^{-1} .

In $\text{Mo}_2(\text{fhp})_4$ we see only a single band with a maximum at 20 100 cm^{-1} . There are poorly defined but reproducible wiggles on the low-energy side of this band, which seemed likely to be due to a vibrational progression comprising ex-

(16) Andersen, R. A.; Jones, R. A.; Wilkinson, G.; Hursthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Chem. Commun.* 1977, 283.

Table V. Selected Bond Distances and Angles for $M_2(\text{fhp})_4(\text{THF})^a$

	M = Cr	M = Mo	M = W
Bond Distances (Å)			
M(1)–M(2)	2.150 (2)	2.092 (1)	2.185 (2)
M(1)–O	2.266 (6)	2.528 (5)	2.49 (2)
M(1)–O(1)	1.974 (7)	2.083 (4)	2.04 (2)
M(1)–O(2)	1.987 (7)	2.066 (4)	2.06 (2)
M(1)–O(3)	1.968 (6)	2.070 (4)	2.06 (2)
M(1)–O(4)	2.006 (7)	2.090 (4)	2.49 (2)
M(2)–N(1)	2.071 (7)	2.170 (5)	2.16 (2)
M(2)–N(2)	2.053 (7)	2.169 (5)	2.15 (2)
M(2)–N(3)	2.087 (7)	2.164 (4)	2.11 (2)
M(2)–N(4)	2.048 (7)	2.151 (4)	2.19 (2)
F(1)–C(5)	1.328 (11)	1.321 (8)	1.34 (4)
F(2)–C(10)	1.340 (11)	1.351 (7)	1.37 (4)
F(3)–C(15)	1.335 (12)	1.378 (8)	1.37 (3)
F(4)–C(20)	1.342 (12)	1.329 (8)	1.27 (3)
O(1)–C(1)	1.261 (13)	1.281 (7)	1.31 (3)
O(2)–C(6)	1.284 (10)	1.298 (6)	1.25 (3)
O(3)–C(11)	1.278 (11)	1.295 (7)	1.25 (3)
O(4)–C(16)	1.275 (12)	1.263 (7)	1.31 (3)
N(1)–C(1)	1.377 (12)	1.385 (8)	1.41 (4)
N(1)–C(5)	1.323 (12)	1.318 (8)	1.39 (4)
N(2)–C(6)	1.368 (11)	1.367 (7)	1.43 (3)
N(2)–C(10)	1.371 (11)	1.309 (7)	1.29 (3)
N(3)–C(11)	1.382 (12)	1.370 (8)	1.40 (3)
N(3)–C(15)	1.325 (12)	1.331 (8)	1.33 (3)
N(4)–C(16)	1.356 (12)	1.373 (7)	1.38 (3)
N(4)–C(20)	1.346 (12)	1.361 (7)	1.32 (3)
Bond Angles (deg)			
M(2)–M(1)–O	179.1 (2)	177.7 (1)	177.1 (6)
–O(1)	91.6 (2)	94.4 (1)	93.7 (5)
–O(2)	91.8 (2)	95.0 (1)	93.2 (5)
–O(3)	92.3 (2)	94.5 (1)	93.2 (5)
–O(4)	91.6 (2)	93.4 (1)	92.8 (5)
M(1)–M(2)–N(1)	91.7 (2)	90.8 (1)	89.0 (7)
–N(2)	91.3 (2)	90.3 (1)	90.3 (5)
–N(3)	90.9 (2)	90.6 (1)	89.7 (6)
–N(4)	91.6 (2)	91.1 (1)	90.5 (6)
M(1)–O(1)–C(1)	122.9 (6)	120.5 (4)	123 (2)
M(1)–O(2)–C(6)	122.4 (6)	119.7 (3)	122 (2)
M(1)–O(3)–C(11)	123.8 (6)	120.2 (4)	120 (2)
M(1)–O(4)–C(16)	121.2 (6)	120.7 (4)	123 (2)
M(2)–N(1)–C(1)	114.9 (7)	116.7 (4)	120 (2)
–C(5)	125.8 (6)	125.7 (5)	124 (2)
C(1)–N(1)–C(5)	119.3 (8)	117.6 (6)	116 (3)
M(2)–N(2)–C(6)	117.3 (6)	117.1 (3)	115 (2)
–C(10)	126.2 (6)	126.0 (4)	127 (2)
C(6)–N(2)–C(10)	116.5 (8)	116.8 (5)	118 (3)
M(2)–N(3)–C(11)	116.3 (6)	117.1 (4)	117 (2)
M(2)–N(3)–C(15)	123.5 (8)	126.5 (5)	128 (2)
C(11)–N(3)–C(15)	120.1 (9)	116.3 (5)	114 (2)
M(2)–N(4)–C(16)	116.9 (7)	116.9 (4)	117 (2)
–C(20)	126.3 (7)	125.2 (4)	122 (2)
C(16)–N(4)–C(20)	116.8 (9)	117.8 (5)	121 (2)
O(1)–C(1)–N(1)	118.8 (8)	117.6 (5)	114 (2)
F(1)–C(5)–N(1)	114.2 (8)	113.0 (6)	112 (3)
O(2)–C(6)–N(2)	117.0 (8)	117.9 (5)	119 (2)
F(2)–C(10)–N(2)	111.0 (7)	112.8 (5)	112 (3)
O(3)–C(11)–N(3)	116.5 (8)	117.5 (5)	120 (3)
F(3)–C(15)–N(3)	114.9 (9)	111.0 (6)	110 (3)
O(4)–C(16)–N(4)	118.7 (9)	117.8 (5)	118 (2)
F(4)–C(20)–N(4)	111.0 (9)	112.8 (6)	116 (3)

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

citations of the Mo–Mo stretching mode in the electronically excited state. From estimates of the spacings between the first five of these features, a vibrational frequency of $380 \pm 40 \text{ cm}^{-1}$ can be extracted. This is not the first time, in compounds of this class, that such a vibrational progression has been noticeable even in the room-temperature spectrum. The first such observation was made by Dubicki and Martin¹⁷ in $\text{Mo}_2(\text{O}_2\text{C}-$

Table VI. Symmetry-Averaged Bond Distances and Angles for $M_2(\text{fhp})_4(\text{THF})^a$

	M = Cr	M = Mo	M = W
Bond Distances (Å)			
M–O(THF)	2.266 (6)	2.528 (5)	2.49 (2)
M–O(fhp)	1.984 [4]	2.077 [2]	2.06 [1]
M–N	2.065 [4]	2.164 [3]	2.15 [1]
F–C	1.336 [7]	1.345 [4]	1.34 [2]
O(coord)–C	1.275 [7]	1.284 [4]	1.28 [2]
N–C(C–O)	1.371 [7]	1.374 [4]	1.41 [2]
N–C(C–F)	1.341 [7]	1.330 [4]	1.33 [2]
Bond Angles (deg)			
M–M–O(THF)	179.1 (2)	177.7 (1)	177.1 (6)
M–M–O(fhp)	91.8 [1]	94.3 [1]	93.2 [3]
M–M–N	91.4 [1]	90.7 [1]	89.9 [3]
M–O–C(fhp)	122.6 [3]	120.3 [2]	122 [1]
M–N–C(C–O)	116.4 [4]	117.0 [2]	117 [1]
M–N–C(C–F)	125.5 [4]	125.9 [3]	125 [1]
C–N–C	118.2 [5]	117.1 [3]	117 [1]
F–C–N	112.8 [5]	112.4 [3]	113 [2]
O–C–N	117.8 [5]	117.7 [3]	118 [1]

^a We use parentheses to represent an esd for a given individual value while brackets represent $[\sum \Delta_i^2/n(n-1)]^{1/2}$, where Δ_i is the deviation of the i th value in a set of n such values from the arithmetic mean of the n values.

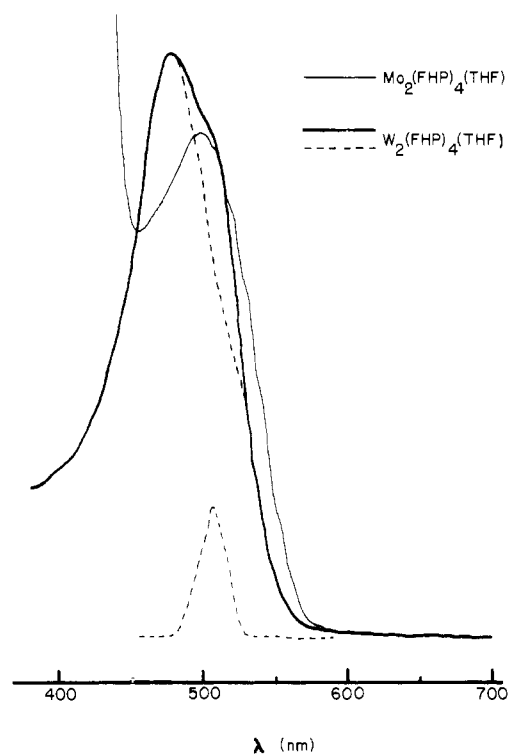


Figure 2. Portions of the visible spectra of $\text{Mo}_2(\text{fhp})_4(\text{THF})$ (—) and $\text{W}_2(\text{fhp})_4(\text{THF})$ (---). The deconvolution of the spectrum of the W compound (---) is only approximate. These spectra were recorded in THF solution at 25 °C.

$\text{CH}_3)_4$ and a remarkably well-defined progression was seen in $\text{K}_3\text{Tc}_2\text{Cl}_8$.¹⁸

We next reexamined this band, using a KBr pellet at 5 K, to see whether this vibrational structure could be measured accurately. We were disappointed to find that although some sharpening of these vibrational features did occur at 5 K, they were still rather broad and more like wiggles than distinct peaks and valleys. The numerical data for the two samples are listed in table VIIB. It must be recognized that, with an

(17) Dubicki, L.; Martin, R. L. *Aust. J. Chem.* **1969**, *22*, 1571.

(18) Cotton, F. A.; Fanwick, P. E.; Gage, L. D.; Kalbacher, B. J.; Martin, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 5642.

Table VII. Electronic Spectral Data for $M_2(fhp)_4(THF)$ and $M_2(mhp)_4$ Compounds of Molybdenum and Tungsten

A. Spectra in THF at 25 °C			
compd	λ/nm	ϵ	assignt
$Mo_2(fhp)_4(THF)$	498	245	$\delta \rightarrow \delta^*$
	400	5600	$\delta \rightarrow \pi_L^*$
$W_2(fhp)_4(THF)$	501 (sh)	300	$\delta \rightarrow \delta^*$
	475	685	$\delta \rightarrow \pi_L^*$
	295	855	

B. Spectra in KBr Pellet at 5 K of $Mo_2(fhp)_4(THF)$					
sample I			sample II		
λ/nm	cm^{-1}	Δ	λ/nm	cm^{-1}	Δ
557.0	17 953		557.5	17 937	
554.5	18 365	412	545.0	18 349	412
534.0	18 727	362	534.0	18 727	378
523.0	19 112	385	525.5	19 066	339
514.0	19 455	343	514.0	19 455	389
505.0	19 802	347	505.0	19 802	347
	av 370 ± 24		495.0	20 202	400
				av 378 ± 23	

C. Spectra in CH_2Cl_2 at 25 °C			
	λ/nm	cm^{-1}	assignt
$Mo_2(mhp)_4$	491	20 400	$\delta \rightarrow \delta^*$
	400	25 000	$\delta \rightarrow \pi_L^*$
$W_2(mhp)_4$	562	17 800	$\delta \rightarrow \delta^*$
	507	19 700	$\delta \rightarrow \pi_L^*$

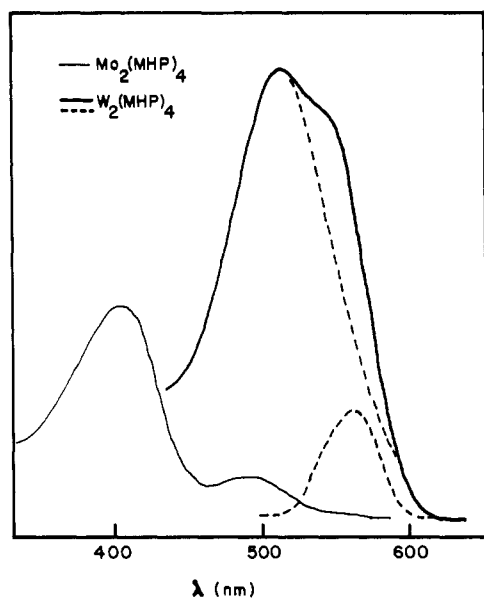


Figure 3. Portions of the visible spectra of $Mo_2(mhp)_4$ (—) and $W_2(mhp)_4$ (---). These spectra were recorded at 25 °C in CH_2Cl_2 solutions. A deconvolution of the $W_2(mhp)_4$ spectrum is shown (---).

error of about ± 0.5 nm in each wavelength, there are uncertainties of ca. 40 cm^{-1} possible for each Δ . Thus, the scatter in the individual values, such that each mean value has a mean deviation of $\pm 24\text{ cm}^{-1}$, is not unexpected. For the two separate spectra the mean values, 370 ± 24 and $378 \pm 23\text{ cm}^{-1}$, agree well with each other and with the value of $380 \pm 40\text{ cm}^{-1}$ estimated from the room-temperature spectrum. These values also compare satisfactorily with the values of $380 \pm 3\text{ cm}^{-1}$ for $Mo_2(mhp)_4$ in a KBr pellet and $344 \pm 11\text{ cm}^{-1}$ for $Mo_2(mhp)_4(THF)_2$ in THF solution recently measured by Fanwick, Bursten, and Kaufman.¹⁹ The band maximum occurs

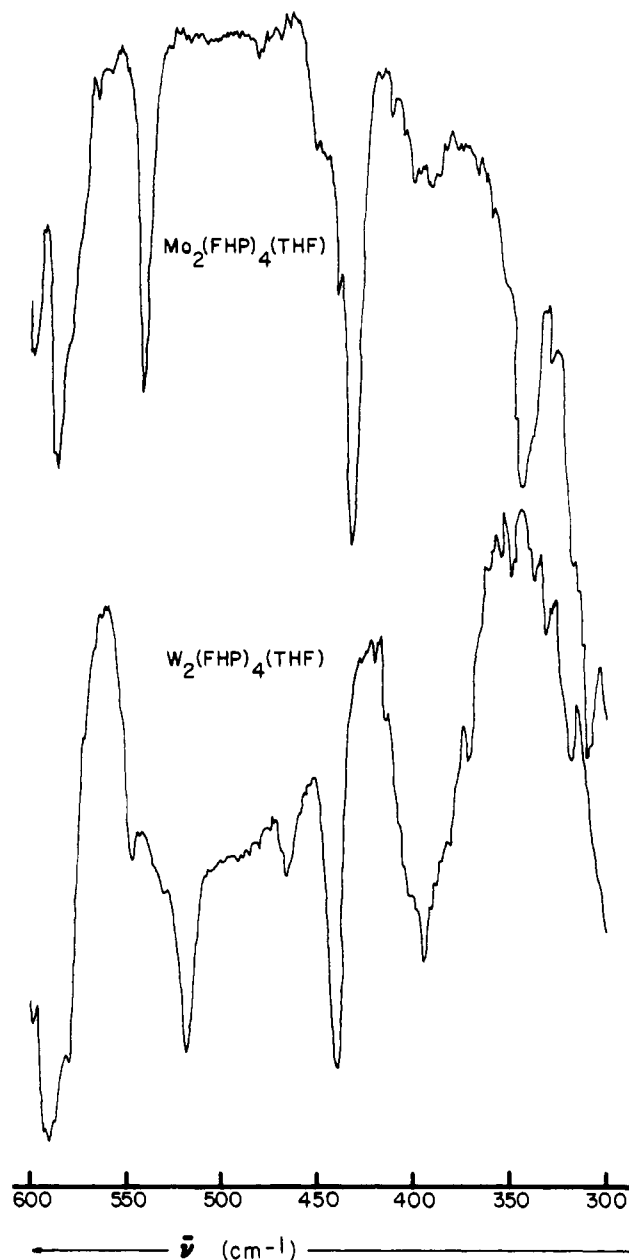


Figure 4. Infrared spectra of $Mo_2(fhp)_4(THF)$ and $W_2(fhp)_4(THF)$ in THF solutions at 25 °C.

at ca. $20\,200\text{ cm}^{-1}$, i.e., at the same energy as that in $Mo_2(mhp)_4$.

There is, in general, a considerable similarity of the spectra of the $M_2(fhp)_4$ and $M_2(mhp)_4$ compounds with $M = Mo$ and W . The spectra of the latter are shown in Figure 3. In each of the $M_2(mhp)_4$ spectra there is a weaker band at lower energy that we believe can be assigned to the $\delta \rightarrow \delta^*$ transition and a stronger one at higher energy that we propose to assign to a $\delta \rightarrow \pi_L^*$ transition as in the case of the $M_2(fhp)_4(THF)$ molecules. The reason that in both cases the $\delta \rightarrow \pi_L^*$ transition is at lower energy for the tungsten compound is that the $W-W$ δ bonding is appreciably weaker than the δ bonding in the molybdenum homologue.²⁰ This results in a smaller energy difference between the δ and π_L^* orbitals. On the whole, it is interesting that, despite the difference in ligand arrangements in the $M_2(fhp)_4$ and $M_2(mhp)_4$ compounds, their bonding and spectroscopic properties are rather similar. A

(19) Fanwick, P. E.; Bursten, B. E.; Kaufman, G. B., submitted for publication in *Inorg. Chem.*

(20) Cotton, F. A.; Hubbard, J. L.; Lichtenberger, D. L.; Shim, I. *J. Am. Chem. Soc.* **1982**, *104*, 679.

comparable spectroscopic comparison is encountered with the $M_2(O_2C\text{-aryl})_4$ molecules of molybdenum and tungsten and will be discussed in detail in a forthcoming publication.²¹

Because the $M_2(fhp)_4$ molecules have polar character with C_{4v} effective symmetry, the M-M stretching vibration is formally active in the infrared spectrum. The frequency of such a band is not subject to much uncertainty. From the bond length, and by comparison to a number of other quadruply bonded dimolybdenum compounds in which ν_{Mo-Mo} is known,²² a frequency of about 425 cm^{-1} would be expected. The only question is whether the vibration will have enough intensity in the infrared region to be observed. We first measured the infrared spectrum of a THF solution of $Mo_2(fhp)_4(THF)$, obtaining the result shown in Figure 4. The strong band at 430 cm^{-1} seemed a reasonable candidate for assignment to the Mo-Mo stretching mode. In an attempt to get supporting evidence, the Raman spectrum was also recorded, but it showed no strong lines in the entire 280-760- cm^{-1} region, and none of the three medium to weak lines at 370, 405, and 643 cm^{-1} matches the 430- cm^{-1} band in the infrared spectrum. Strong lines were recorded at 280 and 760 cm^{-1} and at higher frequencies where ligand-localized vibrations would be expected. We have encountered this problem before with all other $M_2(Xhp)_4$ ligands except the $M_2(mhp)_4$ compounds. No reason for the absence of an intense ν_{M-M} band in these cases has ever been found, but empirically, the present case is in no sense exceptional. As an alternative way of testing the assignment of the 430- cm^{-1} band, the infrared spectrum of the

$W_2(fhp)_4(THF)$ compound was recorded; this too is shown in Figure 4.

Comparison of the two spectra does not lead unambiguously to a decision, but it does provide qualified support for assigning the 430- cm^{-1} band of $Mo_2(fhp)_4(THF)$ to the Mo-Mo stretching mode. If the absorption bands seen in the $W_2(fhp)_4(THF)$ spectrum at ca. 390, 440, and 470 cm^{-1} were reduced in intensity to match absorptions at about those frequencies in $Mo_2(fhp)_4(THF)$ (i.e., by a factor of 3-4) it would be clear that the $W_2(fhp)_4(THF)$ spectrum contains no band comparable in position and relative intensity to the 430- cm^{-1} band of $Mo_2(fhp)_4(THF)$. The change from Mo_2 to W_2 should have as its major effect the shifting of the M-M stretching band from 430 cm^{-1} to a frequency below 300 cm^{-1} (where there is, unfortunately, strong absorption by THF and/or the ligands). We thus think it likely that in this very polar situation the ν_{Mo-Mo} mode of $Mo_2(fhp)_4(THF)$ is being observed in the infrared spectrum.

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Registry No. $Cr_2(fhp)_4(THF)\cdot THF$, 87739-04-6; $Mo_2(fhp)_4(THF)$, 87761-48-6; $W_2(fhp)_4(THF)$, 87739-05-7; $Mo_2(mhp)_4$, 67634-80-4; $W_2(mhp)_4$, 67634-84-8; $Cr_2(O_2CCH_3)_4$, 15020-15-2; $Mo_2(O_2CCH_3)_4$, 14221-06-8; WCl_4 , 13470-13-8; Cr, 7440-47-3; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Tables of temperature factor expressions, bond distances and angles, thermal vibration amplitudes, positional parameters, and observed and calculated structure factors for each compound (76 pages). Ordering information is given on any current masthead page.

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The Chemistry of the 1,2-Dicyanocyclopentadienide Anion: Metal Complexes and Nucleophilic Substitution Reactions

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Reactions of the 1,2-dicyanocyclopentadienide (DCCP) anion with various metal salts have been explored. Stable complexes with silver(I), copper(I), manganese(II), and cobalt(II) have been prepared and analyzed. The crystal structure of the cobalt(II) complex is reported. It crystallizes in the centrosymmetric orthorhombic space group $Pnna$, with cell dimensions $a = 28.538$ (9) Å, $b = 14.044$ (4) Å, $c = 9.017$ (2) Å, $V = 3614$ (2) Å³, and $Z = 4$. Diffraction data were collected with a Syntex P1 diffractometer using $Mo\ K\alpha$ radiation of $\lambda = 0.71069$ Å, and the structure was refined to $R = 0.087$ for 1448 independent reflections. The compound takes the form of a unique cobalt polymer with repeating units defined as $Co[C_5H_3(CN)_2]_4[N(CH_3)_4]_2$. The reaction of the DCCP anion with the 2-(methylthio)-1,3-dithiolium cation results in the formation of the heterosquisfulvalene 2-(3,4-dicyanocyclopentadienylidene)-1,3-dithiole. NMR spectral data imply a large contribution of the dipolar form to the electronic structure of this compound.

Introduction

Donor molecules based on tetrathiafulvalene (TTF)^{1,2} have long been the staple of solid-state chemists interested in new low-dimensional organic electrical conductors.³ Many of the

first conducting solids were combinations of TTF analogues and tetracyano-*p*-quinodimethane (TCNQ).^{4,5}

The acceptor properties of TCNQ,⁶ and cyano-based acceptor molecules in general,⁷ are important for the successful

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