Contribution from Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Homologous Chromium, Molybdenum, and Tungsten Derivatives of 6-Chloro-2-hydroxypyridine. Inductive Effects on the Metal–Metal Bond Length

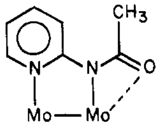
F. ALBERT COTTON,* WILLIAM H. ILSLEY, and WOLFGANG KAIM

Received November 19, 1979

The preparation and structural investigation of the compounds $M_2(chp)_4$, where M = Cr, Mo, and W and chp = the anion of 6-chloro-2-hydroxypyridine (Hchp), are reported. The Cr and Mo compounds were prepared by the reaction of the corresponding acetates, $M_2(O_2CR)_4$, with the lithium salt of Hchp. $W_2(chp)_4$ was obtained by reaction of $W(CO)_6$ with Hchp in refluxing diglyme. The compounds form isomorphous crystals belonging to the orthorhombic space group *Pbca*. Unit cell dimensions (Å) for the Cr, Mo, and W compounds, in that order, are the following: a = 16.078 (2), 16.247 (3), 16.210 (2) Å; b = 18.570 (2), 18.559 (3), 18.583 (3) Å; c = 15.573 (2), 15.827 (2), 15.802 (2) Å. The M–M bond lengths are Cr–Cr = 1.955 (2) Å, Mo–Mo = 2.085 (1) Å, and W–W = 2.177 (1) Å. These distances are all longer than the corresponding distances in the related $M_2(mhp)_4$ compounds (mhp = 6-methyl-2-hydroxypyridine anion). The substitution of chlorine for the methyl group results in a significant increase in the M–M bond length with the greatest increase, 0.066 Å, being found in the chromium compound. This observation leads us to suggest that inductive effects may play an important role in determining the M–M bond distance.

Introduction

Among the ligands that have been found to be suitable for the formation of quadruply bonded compounds of the type M_2L_4, where M = Cr, Mo, or W, the heterocyclic anions of 2-methyl-6-hydroxypyridine (Hmhp) and 2,4-dimethyl-6-hydroxypyrimidine (Hdmhp) are outstanding in several ways: (a) The complexes $M_2(mhp)_4$[1] and $M_2(dmhp)_4$[2] exhibit unusually high thermal stability and inertness toward air. (b) The metal–metal bond distances are among the shortest of their kind. (c) The complexes can be conveniently prepared from the corresponding hexacarbonyls $M(CO)_6$. This preparative procedure is especially important for the quadruply bonded tungsten compounds because $W_2(O_2CR)_4$ species are not available as in the case of Cr and Mo. It is very important in these species to have "blocking groups" like the 6-methyl group of mhp directed toward the axial positions of the complexes to prevent axial interactions, which seem to cause low solubility and hence poorly crystalline materials. Only the blocked compounds have been found to have sufficient solubility and volatility to allow investigations of their structures. The same effect can also be achieved by other "blocking groups" like the phenyl ring in acetanilido compounds $M_2[OC(R)NPh]_4$[3] or in 1,3-diphenyltriazenato complexes $M_2[PhN_3Ph]_4$[4] where M = Cr or Mo. Although the effect of these "blocking groups" appears to be an essentially steric one, preventing axial coordination, there is one case where it seems that the "blocking group" is also able to interact electronically with the metal atom, viz., in tetrakis[*N*-(2-pyridinyl)acetamido]dimolybdenum:[5]



This interaction may be responsible for a significant shortening of the otherwise insensitive Mo–Mo quadruple bond to the shortest value, 2.037 (3) Å, that has yet been observed; the Mo–O intramolecular distance is only 2.849 (15) Å.[5] In an attempt to understand more clearly the factors influencing the metal–metal bond length in these systems we have prepared and examined the crystal structures of the three compounds $M_2(chp)_4$, M = Cr, Mo, or W, where chp is the 6-chloro-2-hydroxypyridine anion. The object was to determine the effect that an electron-withdrawing group would have on the metal–metal bond in contrast to the electron-donating methyl group.

Table I. Crystallographic Data for the $M_2(chp)_4$ Compounds

	$Cr_2(chp)_4$	$Mo_2(chp)_4$	$W_2(chp)_4$
mol wt	618.15	706.04	881.86
a, Å	16.078 (2)	16.247 (3)	16.210 (2)
b, Å	18.570 (2)	18.559 (3)	18.583 (3)
c, Å	15.573 (2)	15.827 (2)	15.802 (2)
$\alpha = \beta = \gamma$, deg	90	90	90
V, Å^3	4650 (2)	4772 (2)	4760 (2)
space group	*Pbca*	*Pbca*	*Pbca*
Z	8	8	8
d_{calcd}, g cm^{-3}	1.766	1.965	2.461
μ, cm^{-1}	14.67	15.13	107.17
data with $I \geq 3\sigma(I)$	1524	2179	1537
R_1	0.051	0.037	0.037
R_2	0.065	0.052	0.046
esd (observn of unit wt)	1.501	1.345	0.999
crystal dimens, mm	0.15 × 0.20 × 0.25	0.30 × 0.30 × 0.30	0.10 × 0.10 × 0.20

Experimental Section

Preparations. The complexes $M_2(chp)_4$ have been synthesized according to procedures very similar to those previously published for the $M_2(mhp)_4$ and $M_2(map)_4$[6] (Hmap = 2-amino-6-methylpyridine) compounds. The Cr and Mo compounds were obtained by the reaction of the corresponding acetates with the anion of 6-chloro-2-hydroxypyridine, and the W compound was obtained by the reaction of 6-chloro-2-hydroxypyridine with $W(CO)_6$. It should be noted, however, that the chp complexes are less soluble than the 6-methyl-substituted analogues, $M_2(mhp)_4$, and therefore a large amount of solvent has to be used in the preparation. Crystals were obtained by slow diffusion of a hexane layer into a saturated THF solution of the complex.

Mass Spectra. A high-resolution mass spectrum was obtained for the ditungsten complex $W_2(chp)_4$ at 270 °C and 10^{-6} torr. The parent ion line group exhibits the characteristic isotope distribution pattern that agrees well with the calculated pattern (see Figure 1). The high-resolution experiment gave a value of 879.854 89 for one of the prominent peaks, the calculated mass of $C_{20}H_{12}Cl_4N_4O_4W_2$ is 879.859 06. The calculated spectrum was obtained by using a program written by Dr. M. W. Extine.

X-ray Data Collection. Suitable crystals of the compounds were coated with epoxy cement, secured to the end of a thin glass fiber with epoxy cement, and mounted on an Enraf-Nonius CAD-4F au-

---

[1] Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

[2] Cotton, F. A.; Niswander, R. H.; Sekutowski, J. C. *Inorg. Chem.* **1979**, *18*, 1152.

[3] Bino, A.; Cotton, F. A.; Kaim, W. *J. Am. Chem. Soc.* **1979**, *101*, 2506.

[4] Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.* **1979**, *18*, 1143.

[5] Cotton, F. A.; Ilsley, W. H.; Kaim, W. *Inorg. Chem.* **1979**, *18*, 2717.

[6] Cotton, F. A.; Niswander, R. H.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3541.

0020-1669/80/1319-1453$01.00/0

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2(chp)_4$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	0.3313 (1)	0.41944 (8)	0.3725 (1)	2.74 (6)	2.96 (6)	2.37 (6)	0.00 (6)	0.08 (7)	−0.01 (7)
Cr(2)	0.2966 (1)	0.31859 (8)	0.3749 (1)	3.29 (7)	2.68 (6)	2.54 (6)	−0.16 (6)	0.23 (7)	−0.07 (7)
Cl(16)	0.3482 (2)	0.5617 (1)	0.2548 (2)	8.4 (2)	3.7 (1)	4.5 (1)	−1.7 (1)	−0.2 (2)	0.4 (1)
Cl(26)	0.1379 (2)	0.2120 (2)	0.3884 (2)	6.8 (2)	3.7 (1)	8.5 (2)	−1.4 (1)	0.5 (2)	−0.3 (2)
Cl(36)	0.3654 (2)	0.1552 (2)	0.3886 (2)	7.4 (2)	3.4 (1)	6.0 (2)	0.2 (1)	2.5 (1)	0.3 (1)
Cl(46)	0.4065 (2)	0.5482 (1)	0.4853 (2)	4.1 (1)	3.4 (1)	3.9 (1)	−0.4 (1)	0.1 (1)	0.0 (1)
O(1)	0.2803 (4)	0.3076 (3)	0.2488 (4)	3.3 (3)	3.4 (3)	3.4 (3)	−0.2 (3)	−0.2 (3)	−0.5 (3)
O(2)	0.2206 (4)	0.4630 (3)	0.3917 (4)	3.4 (3)	2.8 (3)	4.0 (3)	0.1 (3)	0.3 (3)	−0.2 (3)
O(3)	0.4502 (4)	0.4023 (3)	0.3489 (4)	2.4 (3)	3.8 (3)	3.7 (3)	−0.3 (3)	0.3 (3)	0.0 (3)
O(4)	0.3045 (4)	0.3030 (3)	0.4996 (4)	4.7 (4)	2.8 (3)	3.0 (3)	−0.4 (3)	0.2 (3)	0.5 (3)
N(1)	0.3111 (5)	0.4264 (4)	0.2427 (5)	3.4 (4)	3.1 (3)	2.4 (3)	−0.2 (3)	−0.0 (3)	0.2 (3)
N(2)	0.1732 (5)	0.3476 (4)	0.3890 (5)	2.4 (3)	2.7 (3)	3.9 (4)	−0.4 (3)	−0.1 (3)	−0.9 (3)
N(3)	0.4188 (5)	0.2847 (4)	0.3638 (5)	3.2 (4)	3.3 (3)	2.8 (4)	0.6 (3)	0.3 (3)	0.1 (3)
N(4)	0.3540 (4)	0.4176 (4)	0.5021 (5)	2.1 (3)	3.6 (4)	2.4 (3)	−0.5 (3)	0.1 (3)	0.3 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(11)	0.2906 (6)	0.3637 (5)	0.2019 (6)	3.2 (2)	C(31)	0.4769 (6)	0.3371 (5)	0.3499 (6)	3.5 (2)
C(12)	0.2787 (6)	0.3638 (5)	0.1097 (6)	3.3 (2)	C(32)	0.5629 (7)	0.3189 (6)	0.3370 (7)	4.5 (3)
C(13)	0.2867 (7)	0.4260 (5)	0.0667 (7)	3.8 (2)	C(33)	0.5851 (8)	0.2464 (7)	0.3418 (8)	5.7 (3)
C(14)	0.3085 (6)	0.4920 (5)	0.1084 (6)	3.7 (2)	C(34)	0.5248 (8)	0.1945 (6)	0.3593 (8)	5.6 (3)
C(15)	0.3206 (6)	0.4873 (5)	0.1961 (6)	3.2 (2)	C(35)	0.4452 (7)	0.2166 (5)	0.3667 (7)	4.0 (2)
C(21)	0.1582 (6)	0.4197 (5)	0.3927 (6)	3.2 (2)	C(41)	0.3352 (6)	0.3557 (5)	0.5450 (6)	3.1 (2)
C(22)	0.0744 (7)	0.4457 (6)	0.4006 (7)	4.9 (3)	C(42)	0.3509 (7)	0.3485 (5)	0.6353 (7)	3.9 (2)
C(23)	0.0084 (9)	0.3956 (7)	0.4061 (9)	6.5 (3)	C(43)	0.3875 (7)	0.4060 (6)	0.6750 (8)	4.6 (3)
C(24)	0.0265 (8)	0.3209 (7)	0.3994 (8)	6.1 (3)	C(44)	0.4066 (7)	0.4719 (6)	0.6327 (7)	4.3 (2)
C(25)	0.1089 (7)	0.3010 (6)	0.3919 (7)	4.5 (3)	C(45)	0.3877 (6)	0.4728 (5)	0.5469 (6)	2.9 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

tomatic diffractometer. Intensity data were collected by using Mo Kα radiation ($\lambda_{\bar{\alpha}}$ = 0.71073 Å) monochromatized by a graphite crystal in the incident beam. The takeoff angle of the X-ray tube was 2.80° and the temperature during data collection was 26 ± 2 °C. Twenty-five reflections in the range $12.6° < \theta < 15.8°$ were located by using the standard CAD-4 random automatic searching routine. These reflections were subsequently centered and used as input for the standard CAD-4 indexing routine.

The three compounds were found to crystallize in the orthorhombic system, and systematic absences indicated that the space group is *Pbca*. The crystallographic data are listed in Table I.

The intensity data were collected in the range $0 < 2\theta \leq 45°$ with all reflections measured by using an ω–2θ motion. The scan width for each reflection was determined as 0.8 + 0.347(tan θ), and each reflection was measured with a preliminary scan rate of 20.12°/min. The scan rate for the final scan was calculated from the preliminary scan such that the ratio $I/\sigma(I)$ would be at least 20 and the maximum scan time would not exceed 30 s. If in the preliminary scan $I/\sigma(I) \geq 20$, this measurement was used as the datum. The scan rates used varied from 20.12 to 2.51°/min. The width of the adjustable vertical aperture at the detector was given by (1.5 + tan θ) mm. The horizontal slit was 4 mm. Of the 96 steps in the profile scan, the first and last 16 steps were considered to be background. Intensities and standard deviations on the intensities were assigned as

$$I = [P - 2(B_1 + B_2)]S$$

$$\sigma(I) = [P + 4(B_1 + B_2)]^{1/2}S$$

where P is the gross peak intensity, B_1 and B_2 are the background intensities, and S is the scan rate. During data collection, three orientation standards as well as three intensity standards were measured every 100 reflections. The intensity standards showed no significant decrease in intensity throughout data collection so no decay corrections were applied. Lorentz and polarization corrections were applied.[7] In the case of the tungsten compound an empirical absorption correction was applied on the basis of ψ scans at $\chi = 90°$. A total of eight curves were collected. Each curve was collected in 10° intervals from $0 \leq \psi \leq 360°$. The minimum, maximum, and average transmission factors were 84.91, 99.75, and 96.92%.

Solution and Refinement. When it was recognized that the compounds $M_2(chp)_4$, M = Cr, Mo, or W, were isomorphous with the corresponding rhodium compound,[8] refinement was commenced immediately by using the atomic parameters found for the rhodium compound. Full-matrix anisotropic refinement of the metal, oxygen, and nitrogen atoms, and isotropic refinement of the carbon atoms gave the final structural parameters summarized in Tables II–IV. The discrepancy factors R_1 and R_2 are given by

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$$

The function $\sum w(|F_o| - |F_c|)^2$ was minimized with the weighting factor,

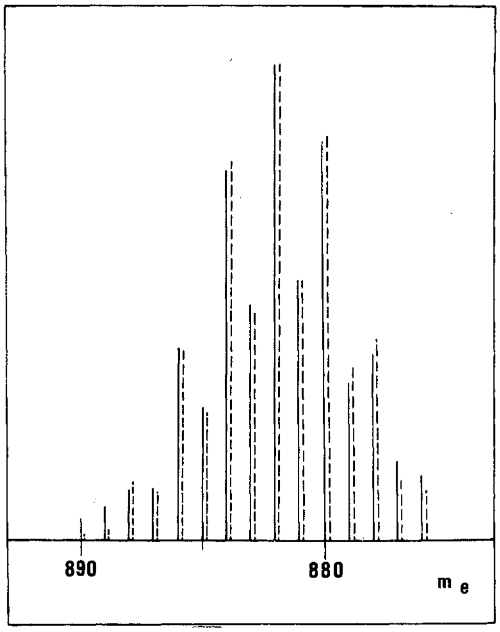


Figure 1. The observed (—) and calculated (---) parent-ion multiplet in the mass spectrum of $W_2(chp)_4$. The mass numbers are given on the horizontal axis, and the height of each line is proportional to the percentage of the entire multiplet intensity that it represents.

---

(7) Calculations were performed by using the Molecular Structure Corp. PDP-11/45 computer and the Enraf-Nonius structure determination package with programs written chiefly by Frenz and Okaya.

(8) Cotton, F. A.; Felthouse, T. to be submitted for publication in *Inorg. Chem.*

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2(chp)_4$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.33119 (4)	0.42207 (3)	0.37197 (3)	2.72 (2)	2.32 (2)	2.50 (2)	−0.18 (2)	0.05 (2)	0.04 (2)
Mo(2)	0.29496 (4)	0.31430 (3)	0.37494 (4)	2.96 (2)	2.21 (2)	2.78 (2)	−0.13 (2)	0.28 (2)	−0.08 (2)
Cl(16)	0.3458 (2)	0.56220 (10)	0.2497 (1)	8.4 (1)	3.39 (9)	4.55 (9)	−1.65 (9)	−0.0 (1)	0.65 (9)
Cl(26)	0.1322 (1)	0.21055 (11)	0.3919 (2)	5.5 (1)	3.25 (9)	8.9 (1)	−1.23 (9)	0.6 (1)	0.1 (1)
Cl(36)	0.3716 (1)	0.15114 (11)	0.3885 (1)	6.6 (1)	3.04 (9)	5.6 (1)	0.24 (9)	2.29 (9)	0.28 (8)
Cl(46)	0.4074 (1)	0.54971 (9)	0.4899 (1)	3.86 (8)	3.01 (8)	4.00 (8)	−0.51 (7)	0.10 (7)	0.10 (7)
O(1)	0.2775 (3)	0.3070 (2)	0.2438 (3)	3.5 (2)	2.8 (2)	3.1 (2)	−0.4 (2)	−0.2 (2)	−0.6 (2)
O(2)	0.2130 (3)	0.4630 (2)	0.3908 (3)	2.8 (2)	2.4 (2)	3.9 (2)	−0.2 (2)	0.2 (2)	−0.3 (2)
O(3)	0.4551 (3)	0.3995 (2)	0.3480 (3)	2.9 (2)	3.2 (2)	3.8 (2)	−0.4 (2)	0.5 (2)	−0.2 (2)
O(4)	0.3080 (3)	0.3026 (2)	0.5048 (3)	4.3 (2)	2.5 (2)	3.0 (2)	−0.1 (2)	0.3 (2)	0.2 (2)
N(1)	0.3104 (3)	0.4260 (3)	0.2384 (3)	2.5 (2)	3.4 (3)	2.4 (2)	−0.2 (2)	0.0 (2)	0.1 (2)
N(2)	0.1687 (3)	0.3466 (3)	0.3902 (3)	2.6 (2)	2.3 (2)	3.7 (3)	−0.1 (2)	0.2 (2)	−0.2 (2)
N(3)	0.4221 (4)	0.2810 (3)	0.3605 (3)	3.7 (3)	2.6 (2)	2.8 (2)	0.6 (2)	0.0 (2)	−0.1 (2)
N(4)	0.3550 (3)	0.4179 (3)	0.5056 (3)	2.5 (2)	2.8 (2)	2.3 (2)	−0.2 (2)	0.2 (2)	0.0 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(11)	0.2885 (4)	0.3632 (4)	0.1978 (4)	3.1 (1)	C(31)	0.4803 (4)	0.3341 (4)	0.3486 (4)	3.2 (1)
C(12)	0.2764 (4)	0.3631 (4)	0.1083 (4)	3.5 (2)	C(32)	0.5645 (5)	0.3155 (4)	0.3351 (5)	4.5 (2)
C(13)	0.2855 (5)	0.4261 (4)	0.0638 (5)	3.8 (2)	C(33)	0.5882 (6)	0.2445 (5)	0.3411 (6)	5.8 (2)
C(14)	0.3069 (5)	0.4919 (4)	0.1054 (4)	3.8 (2)	C(34)	0.5277 (6)	0.1907 (5)	0.3595 (5)	5.3 (2)
C(15)	0.3199 (4)	0.4860 (4)	0.1917 (4)	3.3 (1)	C(35)	0.4485 (4)	0.2132 (4)	0.3666 (4)	3.4 (1)
C(21)	0.1507 (4)	0.4195 (4)	0.3943 (4)	3.3 (1)	C(41)	0.3395 (4)	0.3555 (4)	0.5476 (4)	2.9 (1)
C(22)	0.0698 (5)	0.4442 (5)	0.4033 (5)	5.1 (2)	C(42)	0.3554 (5)	0.3489 (4)	0.6362 (4)	4.1 (2)
C(23)	0.0059 (6)	0.3931 (5)	0.4080 (6)	6.0 (2)	C(43)	0.3893 (5)	0.4067 (4)	0.6763 (5)	5.1 (2)
C(24)	0.0234 (6)	0.3189 (5)	0.4035 (6)	5.9 (2)	C(44)	0.4079 (5)	0.4722 (4)	0.6329 (4)	4.2 (2)
C(25)	0.1046 (5)	0.3003 (4)	0.3956 (4)	3.9 (2)	C(45)	0.3880 (4)	0.4734 (4)	0.5495 (4)	2.9 (1)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations for $W_2(chp)_4$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	0.33218 (5)	0.42434 (4)	0.37231 (6)	3.02 (3)	2.41 (3)	2.89 (3)	−0.20 (3)	−0.04 (4)	0.00 (4)
W(2)	0.29377 (5)	0.31211 (4)	0.37552 (6)	3.30 (3)	2.29 (3)	3.22 (3)	−0.15 (3)	0.24 (4)	−0.08 (4)
Cl(16)	0.3473 (4)	0.5628 (3)	0.2492 (4)	8.5 (4)	3.4 (2)	5.3 (3)	−1.2 (3)	−0.3 (3)	0.8 (3)
Cl(26)	0.1313 (4)	0.2108 (3)	0.3936 (5)	6.2 (3)	3.5 (2)	9.7 (5)	−1.2 (3)	0.5 (3)	0.5 (3)
Cl(36)	0.3699 (4)	0.1505 (3)	0.3883 (4)	7.0 (3)	3.5 (2)	5.9 (3)	0.6 (2)	2.3 (3)	0.3 (3)
Cl(46)	0.4075 (4)	0.5503 (3)	0.4899 (3)	4.8 (3)	2.8 (2)	3.9 (2)	−0.5 (2)	0.2 (2)	−0.0 (2)
O(1)	0.2771 (8)	0.3076 (6)	0.2453 (8)	4.1 (7)	2.8 (5)	2.9 (6)	−0.8 (5)	0.4 (5)	−0.0 (5)
O(2)	0.2134 (7)	0.4632 (6)	0.3912 (8)	2.2 (5)	3.4 (6)	5.2 (7)	0.7 (5)	0.5 (6)	−0.4 (6)
O(3)	0.4549 (8)	0.3998 (6)	0.3488 (7)	3.9 (6)	3.1 (6)	3.2 (7)	−0.0 (5)	−0.3 (5)	0.1 (5)
O(4)	0.3082 (8)	0.3033 (6)	0.5038 (8)	4.9 (7)	3.1 (6)	2.9 (6)	0.6 (6)	0.2 (5)	1.3 (5)
N(1)	0.3102 (9)	0.4253 (8)	0.2423 (10)	3.4 (8)	2.8 (6)	3.1 (7)	−0.8 (6)	−0.7 (6)	0.6 (7)
N(2)	0.1692 (9)	0.3457 (8)	0.3919 (9)	2.2 (6)	3.4 (7)	3.4 (8)	−0.7 (6)	0.8 (7)	0.1 (6)
N(3)	0.4199 (10)	0.2826 (7)	0.3622 (9)	4.7 (8)	2.7 (6)	2.3 (7)	1.5 (6)	−0.6 (7)	−0.8 (6)
N(4)	0.3556 (9)	0.4191 (8)	0.5062 (10)	3.9 (8)	2.6 (7)	3.2 (7)	−0.1 (7)	0.2 (6)	−0.2 (6)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(11)	0.288 (1)	0.3641 (10)	0.199 (1)	3.8 (5)	C(31)	0.481 (1)	0.3306 (10)	0.351 (1)	3.0 (4)
C(12)	0.277 (1)	0.3621 (9)	0.110 (1)	3.5 (4)	C(32)	0.562 (1)	0.3160 (11)	0.334 (1)	4.2 (5)
C(13)	0.284 (1)	0.4235 (11)	0.064 (1)	4.1 (5)	C(33)	0.585 (2)	0.2435 (12)	0.341 (2)	5.5 (6)
C(14)	0.309 (1)	0.4903 (10)	0.104 (1)	3.6 (4)	C(34)	0.527 (1)	0.1883 (11)	0.356 (1)	5.1 (5)
C(15)	0.322 (1)	0.4888 (12)	0.192 (1)	4.9 (5)	C(35)	0.447 (1)	0.2122 (10)	0.367 (1)	3.7 (4)
C(21)	0.154 (1)	0.4191 (10)	0.395 (1)	3.1 (4)	C(36)	0.338 (1)	0.3570 (10)	0.548 (1)	2.8 (4)
C(22)	0.070 (1)	0.4457 (11)	0.403 (1)	3.7 (5)	C(42)	0.356 (1)	0.3505 (11)	0.637 (1)	4.1 (4)
C(23)	0.006 (2)	0.3958 (14)	0.411 (2)	6.4 (7)	C(43)	0.389 (2)	0.4078 (14)	0.677 (2)	5.8 (6)
C(24)	0.020 (2)	0.3179 (13)	0.408 (2)	6.0 (6)	C(44)	0.408 (1)	0.4736 (11)	0.633 (1)	4.7 (5)
C(25)	0.102 (1)	0.2999 (11)	0.399 (1)	4.4 (5)	C(45)	0.389 (1)	0.4725 (10)	0.549 (1)	3.2 (4)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

w, equal to $4F_o^2/\sigma(F_o^2)^2$. All structure factor calculations and least-squares refinements were executed by using only those reflections for which $F_o^2 > 3\sigma(F_o^2)$. The atomic scattering factors were those of Cromer and Waber.[9] Anomalous dispersion effects were included in the scattering factors of tungsten. The observed and calculated structure factors are available as supplementary material.

Results

The three compounds, $M_2(chp)_4$, where M = Cr, Mo, or W, give unsolvated isomorphous crystals. The $M_2(chp)_4$ molecules reside on general positions in the unit cell and as a result have no crystallographically imposed symmetry. Figure 2 shows the $Cr_2(chp)_4$ molecule and defines the atomic numbering scheme used for all three molecules. Tables II–IV give the atomic positional and thermal parameters for the Cr, Mo, and W compounds, respectively. Tables V and VI give the bond distances and bond angles for the three compounds. The molecular structures of the $M_2(chp)_4$ compounds are qualitatively identical with those of the $M_2(mhp)_4$ compounds, differing only in the replacement of the methyl group by a chlorine atom. The ligands are arranged so that the M–N and

---

[9] Cromer, D. T.; Waber, J. T. "International Tables of X-ray Crystallography"; Kynoch Press, Birmingham, England, 1974; Vol IV, Table 2.3.1.

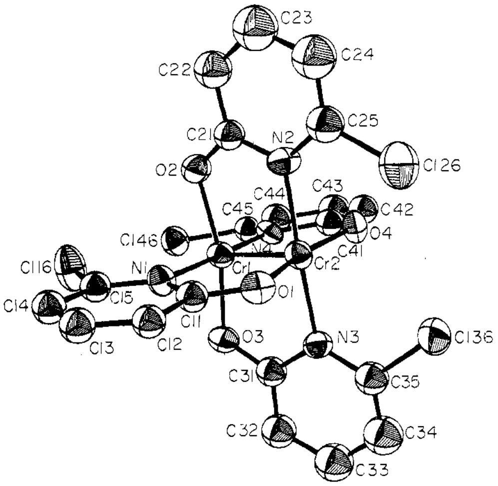


Figure 2. An ORTEP drawing of the $Cr_2(chp)_4$ molecule in which each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50% of the electron density. The atomic numbering scheme is shown and applies to the Mo and W compounds as well.

Table V. Bond Distances for $M_2(chp)_4$

	distance, Å		
atoms	M = Cr	M = Mo	M = W
M(1)–M(2)	1.955 (2)	2.085 (1)	2.177 (1)
–O(2)	1.978 (6)	2.087 (4)	2.08 (1)
–O(3)	1.973 (6)	2.091 (4)	2.07 (1)
–N(1)	2.051 (7)	2.143 (5)	2.08 (2)
–N(4)	2.052 (6)	2.151 (5)	2.15 (2)
M(2)–O(1)	1.993 (6)	2.099 (4)	2.08 (1)
–O(4)	1.966 (6)	2.078 (4)	2.05 (1)
–N(2)	2.068 (7)	2.150 (5)	2.13 (2)
–N(3)	2.070 (7)	2.168 (5)	2.13 (2)
O(1)–C(11)	1.283 (9)	1.286 (7)	1.29 (2)
O(2)–C(21)	1.286 (9)	1.296 (7)	1.27 (2)
O(3)–C(31)	1.285 (9)	1.279 (7)	1.35 (2)
O(4)–C(41)	1.304 (9)	1.297 (7)	1.31 (2)
N(1)–C(11)	1.37 (1)	1.378 (7)	1.38 (2)
–C(15)	1.35 (1)	1.344 (7)	1.44 (3)
N(2)–C(21)	1.36 (1)	1.386 (8)	1.39 (2)
–C(25)	1.35 (1)	1.353 (8)	1.39 (3)
N(3)–C(31)	1.37 (1)	1.379 (8)	1.34 (2)
–C(35)	1.33 (1)	1.334 (8)	1.38 (2)
N(4)–C(41)	1.36 (1)	1.360 (7)	1.36 (2)
–C(45)	1.35 (1)	1.353 (7)	1.32 (2)
C(11)–C(12)	1.45 (1)	1.429 (9)	1.41 (3)
C(12)–C(13)	1.34 (1)	1.373 (9)	1.36 (3)
C(13)–C(14)	1.43 (1)	1.431 (9)	1.45 (3)
C(14)–C(15)	1.38 (1)	1.386 (8)	1.40 (3)
C(15)–Cl(16)	1.716 (9)	1.738 (7)	1.70 (3)
C(21)–C(22)	1.44 (1)	1.40 (1)	1.44 (3)
C(22)–C(23)	1.42 (1)	1.41 (1)	1.40 (3)
C(23)–C(24)	1.42 (1)	1.41 (1)	1.46 (4)
C(24)–C(25)	1.38 (1)	1.37 (1)	1.37 (3)
C(25)–Cl(26)	1.72 (1)	1.726 (7)	1.73 (2)
C(31)–C(32)	1.44 (1)	1.43 (1)	1.37 (3)
C(32)–C(33)	1.39 (1)	1.38 (1)	1.40 (3)
C(33)–C(34)	1.40 (1)	1.43 (1)	1.42 (3)
C(34)–C(35)	1.35 (1)	1.36 (1)	1.37 (3)
C(35)–Cl(36)	1.75 (1)	1.735 (7)	1.73 (2)
C(41)–C(42)	1.44 (1)	1.432 (8)	1.44 (3)
C(42)–C(43)	1.37 (1)	1.364 (9)	1.35 (3)
C(43)–C(44)	1.42 (1)	1.428 (9)	1.45 (3)
C(44)–C(45)	1.37 (1)	1.358 (8)	1.36 (3)
C(45)–Cl(46)	1.723 (8)	1.731 (6)	1.75 (2)

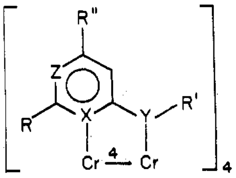
M–O bonds are trans to their own kind with each metal being coordinated to two oxygen and two nitrogen atoms. The idealized molecular symmetry is D_{2d}.

Table VI. Bond Angles for $M_2(chp)_4$

	angle, deg		
atoms	M = Cr	M = Mo	M = W
M(2)–M(1)–O(2)	97.6 (2)	95.0 (1)	93.7 (4)
–O(3)	97.3 (2)	94.8 (1)	93.9 (4)
–N(1)	92.0 (2)	90.6 (1)	89.0 (4)
–N(4)	90.9 (2)	89.7 (1)	89.1 (4)
O(2)–M(1)–O(3)	165.1 (2)	170.0 (2)	172.2 (5)
–N(1)	88.9 (2)	89.0 (2)	88.9 (6)
–N(4)	91.0 (2)	92.2 (2)	92.2 (6)
O(3)–M(1)–N(1)	88.9 (2)	88.8 (2)	89.4 (6)
–N(4)	90.4 (2)	89.9 (2)	89.8 (6)
N(1)–M(1)–N(4)	177.1 (3)	178.7 (2)	177.8 (6)
M(1)–M(2)–O(1)	96.7 (2)	94.5 (1)	93.0 (3)
–O(4)	98.1 (2)	95.4 (1)	93.8 (4)
–N(2)	91.5 (2)	90.3 (1)	89.6 (4)
M(1)–M(2)–N(3)	91.1 (2)	90.1 (1)	88.2 (4)
O(1)–M(2)–O(4)	165.2 (2)	170.1 (2)	173.0 (4)
–N(2)	90.3 (2)	90.0 (2)	90.5 (6)
–N(3)	90.6 (2)	90.3 (2)	91.0 (6)
O(4)–M(2)–N(2)	89.8 (3)	90.9 (2)	90.7 (6)
–N(3)	88.7 (2)	88.7 (2)	88.2 (6)
N(2)–M(2)–N(3)	177.1 (3)	179.5 (2)	177.5 (6)
M(2)–O(1)–C(11)	117.5 (5)	119.2 (4)	120.8 (13)
M(1)–O(2)–C(21)	116.7 (5)	119.8 (4)	119.3 (12)
M(1)–O(3)–C(31)	118.2 (6)	119.8 (4)	120.0 (13)
M(2)–O(4)–C(41)	116.8 (5)	118.4 (4)	120.6 (12)
M(1)–N(1)–C(11)	116.3 (6)	118.2 (4)	122.0 (13)
–C(15)	124.3 (6)	123.6 (4)	122.0 (14)
C(11)–N(1)–C(15)	119.4 (7)	118.3 (5)	116 (2)
M(2)–N(2)–C(21)	115.5 (6)	118.6 (4)	117.6 (13)
–C(25)	124.8 (6)	124.4 (4)	125.3 (14)
C(21)–N(2)–C(25)	119.6 (8)	117.0 (6)	117 (2)
M(2)–N(3)–C(31)	116.5 (6)	117.6 (4)	123.2 (13)
–C(35)	126.0 (6)	124.7 (4)	123.0 (14)
C(31)–N(3)–C(35)	117.5 (8)	117.6 (6)	114 (2)
M(1)–N(4)–C(41)	117.1 (5)	118.5 (4)	118.7 (13)
–C(45)	124.5 (5)	123.4 (4)	122.9 (14)
C(41)–N(4)–C(45)	118.4 (7)	118.1 (5)	118 (2)
O(1)–C(11)–N(1)	117.2 (7)	117.3 (5)	115 (2)
–C(12)	123.3 (8)	122.8 (6)	122 (2)
N(1)–C(11)–C(12)	119.4 (8)	119.9 (6)	123 (2)
C(11)–C(12)–C(13)	118.9 (8)	119.5 (6)	120 (2)
C(12)–C(13)–C(14)	122.3 (8)	121.1 (6)	120 (2)
C(13)–C(14)–C(15)	115.4 (8)	115.0 (6)	117 (2)
Cl(16)–C(15)–N(1)	114.6 (6)	114.3 (4)	113.7 (16)
–C(14)	120.8 (7)	119.5 (5)	123 (2)
N(1)–C(15)–C(14)	124.6 (8)	126.2 (6)	123 (2)
O(2)–C(21)–N(2)	118.4 (8)	116.2 (6)	120 (2)
–C(22)	121.6 (8)	122.2 (6)	120 (2)
N(2)–C(21)–C(22)	120.0 (8)	121.5 (6)	120 (2)
C(21)–C(22)–C(23)	119 (1)	118.5 (8)	118 (2)
C(22)–C(23)–C(24)	119 (1)	120.5 (8)	122.7 (25)
C(23)–C(24)–C(25)	118 (1)	116.5 (8)	113.0 (25)
Cl(26)–C(25)–N(2)	114.1 (7)	114.2 (5)	111.7 (17)
–C(24)	121.4 (9)	119.8 (6)	120 (2)
N(2)–C(25)–C(24)	124.5 (9)	126.0 (7)	128 (2)
O(3)–C(31)–N(3)	116.4 (8)	117.4 (6)	114 (2)
–C(35)	122.8 (8)	122.3 (6)	119 (2)
N(3)–C(31)–C(35)	120.8 (8)	120.3 (6)	127 (2)
C(31)–C(32)–C(33)	117.8 (9)	119.3 (7)	115.6 (22)
C(32)–C(33)–C(34)	120 (1)	119.4 (8)	121.9 (26)
C(33)–C(34)–C(35)	118 (1)	116.9 (7)	114.5 (22)
Cl(36)–C(35)–N(3)	113.0 (7)	114.1 (5)	114.0 (16)
–C(34)	120.9 (8)	119.7 (6)	119.2 (17)
N(3)–C(35)–C(34)	126.0 (9)	126.2 (7)	127 (2)
O(4)–C(41)–N(4)	116.8 (7)	117.6 (5)	117.6 (17)
–C(42)	121.9 (8)	121.1 (6)	122 (2)
N(4)–C(41)–C(42)	121.3 (8)	121.2 (6)	120 (2)
C(41)–C(42)–C(43)	116.5 (8)	117.4 (7)	118.3 (22)
C(42)–C(43)–C(44)	123.8 (9)	122.1 (7)	121.3 (24)
C(43)–C(44)–C(45)	114.5 (8)	115.5 (6)	114.5 (22)
Cl(46)–C(45)–N(4)	113.5 (6)	114.4 (4)	114.8 (16)
–C(44)	121.0 (7)	120.0 (5)	118.1 (17)
N(4)–C(45)–C(44)	125.5 (8)	125.5 (6)	127 (2)

The metal–metal quadruple bond lengths are the features of main interest. For $Mo_2(chp)_4$, the distance is 2.085 (1) Å. This distance is significantly greater than that reported for $Mo_2(DMP)_4$,[3] 2.064 (1) Å, $Mo_2(mhp)_4$,[1] 2.065 (1) Å, or $Mo_2(map)_4$,[6] 2.070 (1) Å. The W–W distance, 2.177 (1) Å,

Table VII. Summary of the Cr–Cr Bond Lengths in Compounds of the Type



compd	X	Y	R	R'	R''	Z	$d_{\mathrm{Cr-Cr}}$, Å	ref
$Cr_2(chp)_4$	N	O	Cl		H	CH	1.955 (2)	*a*
$Cr_2(mhp)_4 \cdot CH_2Cl_2$	N	O	CH_3		H	CH	1.889 (1)	1
$Cr_2(map)_4 \cdot THF$	N	N	CH_3	H	H	CH	1.870 (3)	6
$Cr_2[2,4,6\text{-}(MeO)_3\text{-}C_6H_2]_4$	C	O	CH_3O	CH_3	CH_3O	CH	1.849 (2)	11
$Cr_2[2,6\text{-}(MeO)_2\text{-}C_6H_3]_4$	C	O	CH_3O	CH_3	H	CH	1.847 (2)	15
$Cr_2[2\text{-}MeO\text{-}5\text{-}Me\text{-}C_6H_3]_4$	C	O	H	CH_3	H	CMe	1.828 (2)	14
$Cr_2(dmhp)_4 \cdot O_3C_6H_{14}$	N	O	CH_3		CH_3	N	1.907 (3)	2
$Cr_2(dmhp)_4 \cdot {}^1/_2O_3C_6H_{14}$	N	O	CH_3		CH_3	N	1.898 (3)	2
$Cr_2[PhNC(CH_3)O]_4$	N	O					1.873 (7)	3
$Cr_2[(CH_3N)_2CPh]_4$	N	N					1.843 (2)	16

[a] This work.

is the longest W–W quadruple bond distance reported to date for compounds containing N–C–O bridging ligands. The distance is comparable to the 2.174 (1) Å W–W distance reported for $W_2(dmhp)_2[(PhN)_2CCH_3]_2 \cdot 2THF$,[10] yet significantly longer than the W–W distances found in the $W_2(mhp)_4$, $W_2(dmhp)_4$, and $W_2(map)_4$ structures, which range from 2.155 (2) to 2.164 (1) Å.

The Cr–Cr distance, 1.955 (1) Å, is especially noteworthy. This distance is significantly greater than the Cr–Cr distance reported for $Cr_2(mhp)_4$[1] and related species.[11-14] The implications of this observation will be discussed below. The remaining distances are typical of these systems and as a result nothing further need be said about them.

Discussion

The results obtained in this study derive their chief significance from a comparison with the structures of the analogous $M_2(mhp)_4$ compounds. In both series of compounds axial interactions with other molecules are absent and thus any change in an M–M bond length in going from the mhp to the chp compound must be attributed entirely to intramolecular factors. For all three metal atoms there are increases in the M–M distance when four mhp ligands are replaced by four chp ligands. For Mo_2 and W_2, the increases are very small, which is in keeping with the generally low sensitivity of these quadruple bonds to changes in the character of the ligands and to the presence of axial ligands. Rh_2 complexes show similar small variations.[8] It is with the Cr_2 compound that a large effect is seen, and this will now be discussed in more detail.

The Cr–Cr distance increases by 0.066 (3) Å on going from $Cr_2(mhp)_4$ to $Cr_2(chp)_4$. The entire range of previously known Cr_2 compounds with ligands of this general type (and no axial interactions), as shown by the data summarized in Table VII, is only 0.079 (4) Å, and if we limit the discussion to compounds containing $\overset{\frown}{\mathrm{NO}}$ type ligands, the spread is only 0.034 (8) Å. Thus, the simple replacement of CH_3 by Cl at the 6-position of the 2-oxopyridino ligand has an effect which is among the largest known to occur as a result of making changes other than those involving the axial ligands. The obvious question now is, what is the fundamental cause of this bond-lengthening effect?

Only two possibilities seem to merit consideration. One is that the lone pairs on the chlorine atoms might introduce electron density into the π-antibonding Cr–Cr orbital, thus weakening the bond. We cannot rule this out, even though the Cr···Cl distances have an average value of 3.226 (2) Å, since the Cr–Cr quadruple bond has shown an enormous sensitivity to axial σ interactions.[15] The fact that there are four chlorine atoms, each positioned to provide an electron pair to one lobe of a chromium dπ orbital, could conceivably account for the increase of ca. 0.07 Å.

The other possibility is that we are observing an inductive effect, whereby the replacement of CH_3 by Cl significantly lowers the ionization potential of the lone-pair electrons of the pyridine nitrogen atom, making it more like an oxygen atom. This would be in keeping with the general trend we have already noted,[15] namely, that when not overwhelmed by the more potent influence of changes in the axial ligands, there is a tendency of the Cr–Cr quadruple bond to become longer as the average donor capacity of the right-coordinated ligand atoms is decreased, as when the donor sets are changed from C, O to N, N to N, O.

A decision as to the relative importance of these two possible effects of the 6-Cl atoms may be possible if certain other compounds can be made and characterized structurally. A particularly attractive possibility would be to use the 6-fluoro-2-oxopyridine (fhp) anion as a ligand, since the direct interaction with Cr should be diminished at the same time as the electron-withdrawing effect should be increased. If the inductive effect is controlling, $Cr_2(fhp)_4$ should have a longer Cr–Cr bond than $Cr_2(chp)_4$. We hope to investigate this, as well as several other modifications of the $Cr_2(hp)_4$ type system, in the near future.

Acknowledgment. We thank the National Science Foundation for support. W. Kaim was the recipient of a Liebig Stipend from the Verband der Chemischen Industrie.

Registry No. $Cr_2(chp)_4$, 73274-68-7; $Mo_2(chp)_4$, 73274-69-8; $W_2(chp)_4$, 73274-70-1; $W(CO)_6$, 14040-11-0; $Cr_2(O_2CCH_3)_4$, 15020-15-2; $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Tables of observed and calculated structure factors for the three compounds (24 pages). Ordering information is given on any current masthead page.

---

(10) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *Inorg. Chem.*, in press.
(11) Cotton, F. A.; Millar, M. *Inorg. Chim. Acta* **1977**, *25*, L105.
(12) Cotton, F. A.; Koch, S. A. *Inorg. Chem.* **1978**, *17*, 2021.
(13) Cotton, F. A.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2014.
(14) Cotton, F. A.; Koch, S. A.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2084.
(15) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *J. Am. Chem. Soc.* in press.