Preparation[1a] and Characterization of Chromium(II) Molybdenum(II) Tetraacetate. A Compound Containing a Heteronuclear Quadruple Metal–Metal Bond

C. David Garner,*[1b] Roger G. Senior,[1b] and Trevor J. King[1c]

Contribution from the Chemistry Department, Manchester University, Manchester, M13 9PL, United Kingdom, and the Chemistry Department, Nottingham University, Nottingham, NG7 2RD, United Kingdom. *Received November 3, 1975*

Abstract: The preparation and characterization of the first compound containing a heteronuclear quadruple metal-metal bond, $[CrMo(O_2CCH_3)_4]$, have been achieved. X-Ray crystallographic studies have shown that this compound is isomorphous with $[Mo_2(O_2CCH_3)_4]$, with a triclinic unit cell of space group $P\bar{1}$ and dimensions $a = 8.394$ (1) Å, $b = 5.338$ (1) Å, $c = 7.530$ (1) Å, $\alpha = 84.16$ (2)°, $\beta = 103.38$ (2)°, and $\gamma = 105.13$ (2)° with $Z = 1$. The length of the Cr–Mo bond is 2.050 (1) Å. This dimension is consistent with its formulation as a quadruple metal-metal bond and suggests that the typical length of a Cr≣Cr bond is ca. 2.00 Å. The heteronuclear quadruple metal-metal bond appears to be much more labile than related homonuclear bonds and it is readily cleaved under mild conditions.

Although the dimeric metal(II) carboxylates, $[M_2(O_2CR)_2]$ (where M = Cr,[2-4] Mo,[5-7] Re,[8] Rh,[4,9] or Cu[10]), are well known, remarkably little information has been presented concerning compounds of this or related types containing two different metal atoms. $[MoW(O_2CC(CH_3)_3)_4]$ has been claimed and $[MoW(O_2CC(CH_3)_3)_4I(CH_3CN)]$, with a Mo–W bond order of 3.5, characterized.[11] The ions $[CrMoCl_9]^{3-}$, which may contain strong Cr–Mo interactions, have been synthesized.[12] Here we report the preparation, crystal structure, vibrational spectra, and certain reactions of $[CrMo(O_2CCH_3)_4]$, the first authenticated example of a quadruple heteronuclear metal-metal bond.

Experimental Section

All manipulations were performed under an atmosphere of purified dinitrogen.

Chromium(II) Molybdenum(II) Tetraacetate. $Mo(CO)_6$ (1.64 g, 6.2 mmol) was dissolved in a mixture of acetic acid (120 ml), acetic anhydride (20 ml), and dichloromethane (40 ml) and added dropwise over a period of 8 h to a refluxing solution (at 118 °C) of $[Cr_2(O_2CCH_3)_4(H_2O)_2]$[13] (6.0 g, 16 mmol) dissolved in acetic acid (100 ml) and acetic anhydride (40 ml). The resultant solution was refluxed for a further 16 h, cooled to room temperature, and filtered before the solvent was removed under reduced pressure. A pale yellow precipitate was formed when ca. 150 ml of the solvent remained and this solid was separated by filtration and dried in vacuo to afford $[CrMo(O_2CCH_3)_4]$ in ca. 30% yield (based on $Mo(CO)_6$). A pale yellow reasonably air-stable crystalline solid was obtained by sublimation at 170 °C and 10^{-2} Torr. The compound was found to be only sparingly soluble in water and chloroform but reasonably soluble in pyridine where it formed a red solution.

Anal. Calcd for $C_8H_{12}O_8CrMo$: C, 25.0; H, 3.1; Cr, 13.5; Mo, 25.0. Found: C, 24.6; H, 3.0; Cr, 13.1; Mo, 24.6.

The vibrational spectroscopic data recorded for $[CrMo(O_2CCH_3)_4]$ are presented in Table I. Ir spectra were recorded on a Perkin-Elmer 225 spectrophotometer and Raman spectra on a Cary 82 instrument using 6328 Å laser excitation. The mass spectrum of the compound was obtained on an A.E.I. MS12 instrument using an electron beam of an energy between 70 and 10 eV. The higher m/e values observed in the mass spectrum recorded at this lower energy limit are presented and assigned in Table II.

Carefully controlled sublimation of $[CrMo(O_2CCH_3)_4]$ at <170 °C and 10^{-2} Torr afforded some of this material as needle-like crystals. Some of these crystals were suitable for x-ray diffraction analysis. Many of them, however, were unsuitable due to various twinning problems, some of which only became apparent on upper layer Weissenberg photographs. Crystal data: $C_8H_{12}O_8CrMo$; M = 384.1; triclinic; $a = 8.394$ (1), $b = 5.338$ (1), $c = 7.530$ (1) Å; $\alpha = 84.16$ (2), $\beta = 103.38$ (2), $\gamma = 105.13$ (2)°; $U = 315.2$ Å^3, $Z = 1$, $d_c = 2.02$ g cm^{-3}; $F(000) = 190$, Mo Kα radiation, λ 0.7107 Å, μ(Mo Kα) = 19.0 cm^{-1}; space group $P\bar{1}$.

Preliminary unitcell dimensions and space-group data were obtained from Weissenberg, precession, and oscillation photographs and refined on a Hilger and Watts four-circle diffractometer. The layers $hk0$-10 were explored on the diffractometer for a cylindrical shaped crystal ca. 1.5 mm in length and 0.1 mm in cross-sectional diameter, and 1349 reflections with $I > 3\sigma(I)$ in the range $0 < 2\theta < 62°$ were considered observed and used in the subsequent refinement. No account was taken of anomalous dispersion, and no corrections were made for secondary extinction or absorption; the maximum error introduced by the neglect of absorption effects was estimated to be ca. 10% in F. Data reduction and crystallographic calculations were carried out on the Nottingham University I.C.L. 1906A computer using the Oxford University "CRYSTALS" programs. Atomic scattering factors were used as published.[14] The positions of the metal atoms were located from a three-dimensional Patterson synthesis, and a three-dimensional Fourier synthesis in $P\bar{1}$ symmetry, with molybdenum atoms on both the metal sites, revealed the positions of the two acetato groups in the asymmetric unit. Refinement was then continued in the expected $P1$ symmetry using least-squares procedures and this converged[15] at $R_1 = 0.11$. This level of refinement was considered to be unsatisfactory and further refinement was then attempted in $P\bar{1}$ symmetry, each metal site being occupied by 0.5 Cr and 0.5 Mo atoms. This approach resulted in a significant improvement in the refinement, the final R_1 and R_2 values being 0.053 and 0.067, respectively. In the final difference Fourier the highest peaks were of ca. 1 eÅ^{-3} in density and were in the vicinity of the metal atoms; several peaks of density ca. 0.5 eÅ^{-3} were in positions in which the hydrogen atom would be expected and therefore it was not considered worthwhile to attempt to locate these latter atoms.

The final atomic coordinates and thermal parameters are listed in Table III, the relevant interatomic distances and interbond angles in Table IV, and the important least-squares planes are defined in Table V. A table of structure factors is available.[16]

Reactions of Chromium(II) Molybdenum(II) Tetraacetate. A. $[CrMo(O_2CCH_3)_4]$ (0.48 g, 1.28 mmol) was stirred with a mixture of CF_3CO_2H (5 ml) and $(CF_3CO)_2O$ (0.5 ml) at ca. 25 °C for 16 h. A small amount of a pale green solid ($[Cr(O_2CCF_3)_3]$?) was removed by filtration and the subsequent removal of solvent in vacuo yielded a bright yellow solid which was purified by sublimation (80 °C, 10^{-2} Torr) to give a bright yellow crystalline solid. The analytical data obtained for this solid Cr 5.0% Mo 21.6% was consistent with a mixture of $[CrMo(O_2CCF_3)_4]$ and $[Mo_2(O_2CCF_3)_4]$ in the molar ratio 4:3. The mass spectrum of this material contained, in addition to peaks at m/e values characteristic of $[Mo_2(O_2CCF_3)_4]$, peaks at the following m/e values (for ^{96}Mo) (of the approximate relative intensity) which are tentatively assigned as follows: 600 (8) $[CrMo(O_2CCF_3)_4]^+$, 546 (55) $[CrMo(O_2CCF_3)_3(OCCF)]^+$, 527 (21) $[CrMo(O_2CCF_3)_3(OC_2)]^+$, 506 (11) $[CrMo(O_2CCF_3)_3F]^+$, 492 (69) $[CrMo(O_2CCF_3)_2(OCCF_2)(OC_2)]^+$, 452 (75) [CrMo-

Table I. Vibrational Data (cm^{-1}) for $[CrMo(O_2CCH_3)_4]$

Infrared[a]	Raman[b]	Assignment
1552s		ν_{asym} (OCO)
1525s		
1500s		
1459s	1460m, sh	ν_{sym} (OCO) + $\delta(CH_3)$
	1438s	
1416s, sh	1420m, sh	
1355m	1370w	
1048w		$\rho(CH_3)$
1033w		
940w	952s	ν(C–C)
680s	695s	δ(OCO)
632w		
629w		
580vw		
405w	410m	ν(Cr–O)
393w	394s	ν(Cr–Mo)
387w	385w, sh	ν(Cr–O)
370w	375w	ν(Mo–O)
351w	351vw	
341m		
331w	324m	
	311w, sh	
	301w	
	198m	
	186m	
	168vw	
	128w, sh	
	116m	

[a] Recorded as a KBr disk. [b] Recorded for the powdered solid: s = strong, m = medium, w = weak, sh = shoulder, asym = asymmetric, sym = symmetric.

Table II. Mass Spectrum of $[CrMo(O_2CCH_3)_4]$[a]

m/e (Mo = 96)	Rel intensity	Assignment
384	100	$[CrMo(O_2CCH_3)_4]^+$
356	6	$[CrMo(O_2CCH_3)_3(OCH_3)]^+$
341	16[b]	$[CrMo(O_2CCH_3)_3(O)]^+$
314	45	$[CrMo(O_2CCH_3)_2(OCH_3)(OH)]^+$
298	30[b]	$[CrMo(O_2CCH_3)_2(O)_2]^+$
282	30	$[CrMo(O_2CCH_3)_2(O)]^+$
271	23	$[CrMo(O_2CCH_3)(OCH_3)(OH)(O)]^+$
256	23[b]	$[CrMo(O_2CCH_3)(OH)(O)_2]^+$
239	17	$[CrMo(O_2CCH_3)(O)_2]^+$
197	11[b]	$[CrMo(OH)(O)_2]^+$

[a] Omitting fragments due to $[Mo_2(O_2CCH_3)_4]$. [b] Intensity enhanced by an overlapping $[Mo_2(O_2CCH_3)_4]$ fragment.

$(O_2CCF_3)_2(OCCF_2)]^+$, 433 (25) $[CrMo(O_2CCF_3)_2(OCCF)]^+$, 412 (13) $[CrMo(O_2CCF_3)_2F_2]^+$, 398 (100) $[CrMo(O_2CCF_3)(OCCF_3)(OC_2)]^+$, together with peaks at lower *m/e* values due to further fragmentation of these ions.

The ir spectrum of the yellow crystalline material pressed into a KBr disk was recorded and this contained absorptions at 1615 s, 787 w, 567 w, 443 vw, 429 vw, 394 w, and 314 w cm^{-1}, in addition to absorptions characteristic of $[Mo_2(O_2CCF_3)_4]$.

B. $[CrMo(O_2CCH_3)_4]$ (0.58 g, 1.5 mmol) was stirred at 0 °C for 4 h with a solution of KCl (0.8 g, 10.7 mmol) dissolved in aqueous HCl (50 ml) saturated with HCl gas. A magenta solid was subsequently removed from this mixture by filtration and shown by analyses to be $K_4[Mo_2Cl_8]\cdot H_2O$.

Discussion

Since $[Mo_2(O_2CCH_3)_4]$ is readily prepared by the reaction of $Mo(CO)_6$ with refluxing $CH_3CO_2H/(CH_3CO)_2O$,[5] it was considered that the simplest synthesis of $[CrMo(O_2CCH_3)_4]$ would be by the reaction of a mixture of $Cr(CO)_6$ and $Mo(CO)_6$ in $CH_3CO_2H/(CH_3CO)_2O$. The yellow solid from this reaction mixture was shown to be predominantly $[Mo_2(O_2CCH_3)_4]$ by mass spectral analysis which, however, also revealed a very weak series of fragments with isotopic distribution characteristic of the presence of one molybdenum atom. The highest such peak was observed at *m/e* 384 (Mo = 96) and this was considered to be due to the $[CrMo(O_2CCH_3)_4]^+$ ion. Since the amount of the heteronuclear derivative so produced was too small to allow its separation from $[Mo(O_2CCH_3)_4]$, an alternative synthetic procedure was sought. Cannon and Lund[17] have observed that $[Cr_2(O_2CCH_3)_4]$ is in equilibrium with $[Cr(O_2CCH_3)_2]$ in aqueous solution. Since Mo–Mo quadruple bonds[4] are generally considered to be much stronger than these Cr–Cr bonds, it was surmized that should Cr–Mo quadruple bonds be formed, they would probably be weaker than the former but stronger than the latter. Hence, by the slow addition of $Mo(CO)_6$ to a solution containing a large excess of $[Cr_2(O_2CCH_3)_4]$, it was considered that the production of $[Mo_2(O_2CCH_3)_4]$ should be minimized and that of $[CrMo(O_2CCH_3)_4]$ maximized. This procedure was repeated several times and the conditions described earlier appear to be the optimum for the production of the heteronuclear derivative. The main by-product of the reaction was $[Cr(O_2CCH_3)_3]$ from which the product was readily separated by fractional crystallization. However, all the samples of $[CrMo(O_2CCH_3)_4]$ thus obtained contained some $[Mo_2(O_2CCH_3)_4]$ and further purification by sublimation was necessary.

The characterization of $[CrMo(O_2CCH_3)_4]$ as a pure compound presented some difficulties. The mass spectrum of the compound using a 70-eV electron beam showed not only the mass spectrum of $[CrMo(O_2CCH_3)_4]$ (Table II) but also a slightly weaker mass spectrum characteristic of $[Mo_2(O_2CCH_3)_4]$. The intensity of this latter spectrum was reduced by using a 10-eV electron beam and the dimolybdenum species probably result from decomposition and recombination reactions at the source and/or on ionization in the mass spectrometer. The analytical data obtained for the "pure" material at first consistently suggested that the material was a mixture of $[CrMo(O_2CCH_3)_4]$ and $[Mo_2(O_2CCH_3)_4]$ since the chromium and molybdenum analyses were lower and higher, respectively, than the calculated percentages. However, as vibrational spectroscopic data (vide infra) indicated that the material did *not* contain any $[Mo_2(O_2CCH_3)_4]$, it was considered possible that some of the chromium was being volatilized (as $[CrO_2(O_2CCH_3)_2]$[18]) in the acid digestion stage of the analysis. Consequently, the acid digestion was subsequently accomplished in a sealed bomb and the subsequent atomic absorption analyses were then consistent with the formulation of the material as $[CrMo(O_2CCH_3)_4]$. The vibrational spectra recorded for the compound are presented in Table I; the assignments for the ν(Cr–O) and ν(Mo–O) vibrational modes are made by comparison with the ir spectra of $[Cr(O_2CCH_3)_4\cdot 2H_2O]$[19] and $[Mo_2(O_2CCH_3)_4]$.[20] $[CrMo(O_2CCH_3)_4]$ exhibits a reasonably strong Raman effect at 394 cm^{-1} which is assigned to the vibrational mode which involves Cr–Mo stretching; a weak band at the same frequency is also observed in the ir spectrum. However, the presence of ν(Cr–O) stretching frequencies in the same region of the spectrum suggests that this assignment may not be completely unequivocal. Assuming that the frequencies 406 and 394 represent the stretching of the metal-metal bonds alone in $[Mo_2(O_2CCH_3)_4]$ and $[CrMo(O_2CCH_3)_4]$, respectively, the simple harmonic approximation of vibrational motion suggests

Table III. Final Positional and Anisotropic Thermal Parameters[a] for the Nonhydrogen Atoms of [$CrMo(O_2CCH_3)_4$]

Atom	Site Occupancy	*x/a*	*y/b*	*z/c*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr	0.5	0.0402 (1)	0.1673 (1)	0.0707 (1)	0.01127 (12)	0.01512 (22)	0.01213 (14)	0.00320 (11)	0.00240 (8)	−0.00303 (11)
Mo	0.5	0.0402 (1)	0.1673 (1)	0.0707 (1)	0.01127 (12)	0.01512 (22)	0.01213 (14)	0.00320 (11)	0.00240 (8)	−0.00303 (11)
O(1)	1.0	−0.1767 (7)	0.0827 (9)	0.1732 (7)	0.0157 (10)	0.0237 (10)	0.0171 (11)	0.0063 (10)	0.0049 (8)	−0.0034 (10)
O(2)	1.0	−0.0749 (6)	0.3688 (9)	−0.1564 (7)	0.0146 (9)	0.0213 (16)	0.0147 (8)	0.0038 (9)	0.0032 (8)	−0.0035 (10)
O(3)	1.0	0.2611 (7)	0.2796 (9)	−0.0217 (8)	0.0154 (10)	0.0210 (17)	0.0183 (12)	0.0007 (10)	0.0032 (8)	−0.0019 (11)
O(4)	1.0	0.1587 (7)	−0.0015 (9)	0.3040 (7)	0.0184 (11)	0.0233 (18)	0.0158 (11)	0.0049 (11)	0.0018 (9)	−0.0073 (11)
C(1)	1.0	−0.2835 (10)	−0.1276 (15)	0.1278 (11)	0.0143 (14)	0.0340 (31)	0.0156 (15)	0.0048 (16)	0.0036 (11)	0.0016 (16)
C(2)	1.0	−0.1494 (9)	0.2448 (14)	−0.3015 (10)	0.0138 (12)	0.0288 (19)	0.0124 (12)	0.0049 (14)	0.0022 (10)	−0.0032 (14)
C(3)	1.0	−0.4430 (12)	0.2004 (21)	0.2120 (14)	0.0155 (16)	0.0572 (48)	0.0254 (23)	0.0086 (22)	0.0098 (16)	0.0055 (25)
C(4)	1.0	−0.2266 (13)	0.3849 (19)	−0.4692 (12)	0.0211 (19)	0.0475 (41)	0.0140 (16)	0.0116 (22)	0.0000 (13)	−0.0017 (19)

[a] The numbers in parentheses in this and Table IV are estimated standard deviations in the least significant digits. The anisotropic temperature factors are in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV. Interatomic Distances and Interbond Angles for [$CrMo(O_2CCH_3)_4$[a]

Intramolecular Distances (Å)		Interbond Angles (deg)	
Cr-Mo	2.050 (1)	M′-M-O(1)	91.8 (1)
M-O(1)	2.065 (5)	M′-M-O(2)	90.3 (1)
M-O(2)	2.102 (5)	M′-M-O(3)	92.7 (2)
M-O(3)	2.053 (5)	M′-M-O(4)	94.5 (1)
M-O(4)	2.055 (6)	O(1)-M-O(3)	175.4 (2)
C(1)-O(1)	1.262 (9)	O(2)-M-O(4)	175.2 (2)
C(1)-O(3′)	1.270 (9)	O(1)-M-O(2)	90.4 (2)
C(2)-O(4)	1.283 (8)	O(1)-M-O(4)	89.3 (2)
C(2)-O(2′)	1.280 (8)	O(2)-M-O(3)	89.1 (2)
C(1)-C(3)	1.512 (11)	O(3)-M-O(4)	90.8 (2)
C(2)-C(4)	1.502 (11)	M-O(1)-C(1)	117.0 (4)
		M-O(2)-C(2′)	118.3 (4)
Intermolecular Distance (Å)		M-O(3)-C(1′)	116.4 (4)
M-O(2)	2.548 (4)	M-O(4)-C(2)	116.7 (5)
		O(1)-C(1)-O(3′)	122.0 (7)
		O(4)-C(2)-O(2′)	120.3 (7)
		O(1)-C(1)-C(3)	118.9 (8)
		O(2′)-C(2)-C(4)	119.8 (7)
		O(3′)-C(1)-C(3)	119.1 (8)
		O(4)-C(2)-C(4)	119.9 (7)

Table V. Least-Squares Planes and Dihedral Angles for [$CrMo(O_2CCH_3)_4$]

	Equations[a] of Least-Squares Planes	
(1)	O(1), O(3′), O(1′), O(3)	$3.489x - 2.876y + 4.933z - 0 = 0$
(2)	O(2), O(4), O(2′), O(4′)	$-7.676x + 0.140y + 4.005z - 0 = 0$
(3)	O(1), O(2), O(4), O(4)	$-0.342x + 4.578y + 3.754z - 1.093 = 0$

Dihedral Angles (deg)	
Planes (1) and (2)	90.8
Planes (1) and (3)	91.6
Planes (2) and (3)	89.6

[a] *x*, *y*, and *z* are fractional triclinic coordinates.

that the Cr-Mo stretching force constant is 0.66 times that of the Mo-Mo one.

An x-ray crystal structure was attempted to further characterize [$CrMo(O_2CCH_3)_4$]. This was accomplished despite the relatively small quantity of crystalline material obtained and certain twinning problems observed within these crystals. The compound is isomorphous with [$Mo_2(O_2CCH_3)_4$] and the details of the crystal and molecular structure (Tables III, IV, and V) are presented using the conventions adopted for this latter compound to allow for immediate comparisons. The [$CrMo(O_2CCH_3)_4$] structure contains a statistical disorder of the metal atoms on their sites. It is believed that this disorder simply and only involves a random variation in the sense in which the Cr-Mo vector is arranged along the metal-metal axis of each unit cell, for the following reasons: (i) The vibrational spectroscopic data give no indication of the presence of any [$Mo_2(O_2CCH_3)_4$] molecules which would be obtained in any other disordering of the metal atoms. (ii) The mass spectral data show clearly that discrete [$CrMo(O_2CCH_3)_4$] units *can* exist. (iii) The esd of the Cr-Mo distance and the anisotropic temperature factors associated with the metal atoms are "normal" and certainly lower than would be anticipated if the metal-metal separation was an average of Mo-Mo, Cr-Cr, and Cr-Mo distances.

The most significant feature of the structure is the Cr-Mo separation of 2.050 (1) Å which is shorter than the metal-metal separations in [$Mo_2(O_2CCH_3)_4$] (2.093 (1) Å)[7] and [$Cr(O_2CCH_3)_4{\cdot}2H_2O$] (2.362 (1) Å).[4] This Cr-Mo distance is very close to the mean of the Mo-Mo separation in [$Mo_2(O_2CCH_3)_4$] and the Cr-Cr separations in [$Cr_2(CH_3)_8]^{4-}$ (1.980 (5) Å),[21] [$Cr_2(C_4H_8)_4]^{4-}$ (1.975 (5) Å),[22] and [$Cr_2(C_3H_5)_4$] (1.97 Å).[23] It is thus concluded that the Cr-Mo bond length in [$CrMo(O_2CCH_3)_4$] is clearly consistent with the formulation of this as a metal-metal quadruple bond.[24]

The structural data presently available suggest that a chromium atom contributes ca. 1.00 Å to the length of a quadruple metal-metal bond. This estimate is in good agreement with the value of 1.98 Å "calculated" as the length of a Cr≣Cr bond on the basis of "maximum-valence radii" considerations.[25] Therefore, it is suggested that the metal-metal separation[4] in $[Cr_2(O_2CCH_3)_4{\cdot}2H_2O]$ should *not* be regarded as characteristic of a Cr-Cr quadruple bond.[26]

The average of the metal-oxygen bond lengths (Table IV) within the $[CrMo(O_2CCH_3)_4]$ molecule (2.07 (2) Å) is very close to the average of the corresponding values for $[Cr_2(O_2CCH_3)_4{\cdot}2H_2O]$ (2.018 (8) Å)[4] and $[Mo_2(O_2CCH_3)_4]$ (2.12 (1) Å).[7] The average bond lengths within the acetato groups (C-O = 1.27 (1); C-C = 1.51 (1) Å) agree well with the corresponding details for the $[Mo_2(O_2CCH_3)_4]$[7] and $[Cr_2(O_2CCH_3)_4{\cdot}2H_2O]$[4] structures. As expected in view of the metal-metal separations, the interbond angles, M′-M-O = 92.3 (1.7) and O-C-O = 121.1 (1.2)°, more closely resemble the values found for $[Mo_2(O_2CCH_3)_4]$ than for $[Cr_2(O_2CCH_3)_4{\cdot}2H_2O]$. The $[CrMo(O_2CCH_3)_4]$ molecules are linked together to form infinite chains in the manner described[7] for $[Mo_2(O_2CCH_3)_4]$. The oxygen atoms O(2) and O(2′) each make a contact that is approximately coaxial (O(2)-M-M′ = 161.2 (1)°) with a Cr-Mo bond to the closest metal atom of the adjacent molecule. The O···M distance of 2.548 (4) Å is ca. 0.1 Å shorter than the corresponding distance in $[Mo_2(O_2CCH_3)_4]$.

The anisotropic temperature factors for $[CrMo(O_2CCH_3)_4]$ (Table III) are slightly (~11%) larger than the corresponding[7] values for $[Mo_2(O_2CCH_3)_4]$. This difference probably arises, at least in part, from the metal atom disorder obtained in $[CrMo(O_2CCH_3)_4]$. It is of interest to note that the same general pattern in the relative magnitudes of these temperature factors is observed for these two crystal structure determinations.

The ready cleavage of this Cr≣Mo bond is disappointing. Although $[CrMo(O_2CCF_3)_4]$ has been partially characterized in this study, the number of derivatives containing a Cr≣Mo bond which may be readily obtained appears to be severely limited.

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Supplementary Material Available: A listing of structure factor amplitudes and phases (12 pages). Ordering information is given on any current masthead page.

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Direct Synthesis of Fluorinated Peroxides. 6. The Addition of Fluorinated Hydroperoxides to Perfluoro-2-azapropene and the Preparation of the First Perfluorooxazirine

E. R. Falardeau and D. D. DesMarteau*[1]

Contribution from the Department of Chemistry, Kansas State University, Manhattan, Kansas 66506. *Received July 25, 1975*

Abstract: The addition of CF_3OOH and SF_5OOH to $CF_3N{=}CF_2$ has been observed to result in the formation of $CF_3OOCF_2NHCF_3$ and $SF_5OOCF_2NHCF_3$. Physical and spectral data on the new peroxides are reported including an analysis of the AB_4 portion of the ^{19}F NMR spectrum of $SF_5OOCF_2NHCF_3$. The NaF induced HF elimination from $CF_3OOCF_2NHCF_3$ and $SF_5OOCF_2NHCF_3$ to produce COF_2, SOF_4, NaF·HF, and $CF_3\overline{NCF_2O}$ is discussed.

Several methods for the introduction of the CF_3OO– and SF_5OO– groups into organic molecules have been reported. Both CF_3OOH and SF_5OOH have proven to be valuable in this respect in their reactions with acid halides to produce $RC(O)OOCF_3$ and $RC(O)OOSF_5$.[2,3] The addition of CF_3OOCl,[4] SF_5OOCl,[5] CF_3OOF,[6] and CF_3OOOCF_3[7] to alkenes has also resulted in the convenient direct synthesis of peroxides containing the CF_3OO– or the SF_5OO– groups. However, attempts to add CF_3OOH to a wide variety of alkenes were unsuccessful.[8]