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Carbonyl Scrambling in Azulenehexacarbonyldimolybdenum and Its Tungsten Analogue with Guaiazulene. Structure of Guaiazulenehexacarbonylditungsten

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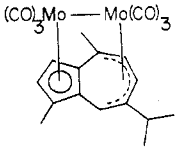
The rate and pathway of CO scrambling in (azl)$Mo_2(CO)_6$ (azl = azulene) have been measured by ^{13}C NMR spectroscopy for comparison with previously published results for the analogous guaiazulene compound. The results are qualitatively the same and show only slightly different rates, in accord with the idea that the presence of alkyl substituents on the azulene ligand has only a small effect upon the fluxional process. The dynamical properties of (gazl)$W_2(CO)_6$ (gazl = guaiazulene) are virtually identical with those of its molybdenum analogue, as is also its crystal structure. Even the metal-to-metal bond distances (Mo–Mo, 3.267 (6) Å; W–W, 3.264 (1) Å) are practically identical.

Introduction

Recently work in this laboratory[1] has shown that each of the two $Mo(CO)_3$ groups in (gazl)$Mo_2(CO)_6$, **1**, scrambles locally and that there is a large difference in their rates of scrambling. A study[2] on the triethylphosphine derivatives of **1**, compounds **2** and **3**, has revealed that it is the $Mo(CO)_3$ group bonded to the cyclopentadienyl portion of the guaiazulene ligand that scrambles fastest. Assuming identical frequency factors (ca. $10^{13.2}$) and identical line separations, this $Mo(CO)_3$ group has an activation energy for local scrambling that is more than 4 kcal mol^{-1} lower than the activation energy for the $Mo(CO)_3$ group bonded to the seven-membered ring of the guaiazulene ligand.



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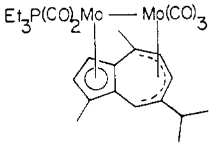

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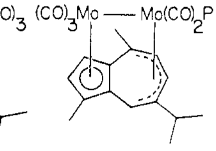

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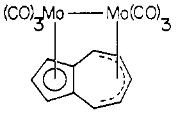

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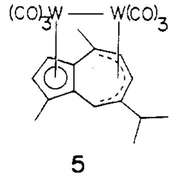

5

In an effort to understand why the two $Mo(CO)_3$ groups in **1** have such disparate rates for local scrambling we have studied the fluxional character of (azl)$Mo_2(CO)_6$, **4**, and (gazl)$W_2(CO)_6$, **5**. Compound **4** allows us to examine the possible effects of the alkyl substituents on the azulene ring on the scrambling processes. Compound **5**, which is the tungsten analogue of compound **1**, allows us to determine whether the rates of scrambling are sensitive to a change from the second to the third transition series.

Experimental Section

(azl)$Mo_2(CO)_6$. This compound, prepared according to the literature,[3] was characterized by ir spectrophotometry (carbonyl bands in CH_2Cl_2: 2030 (s), 1955 (s), 1895 (w), 1870 (w) cm^{-1}) and by its mass spectrum (M^+ = 488 and peaks at 460, 432, 404, 376, 348, and 320 due to successive losses of one carbonyl).

(gazl)$W_2(CO)_6$. A 150-ml, three-neck flask was charged with $(CH_3CN)_3W(CO)_3$ (2.5 g) and guaiazulene (0.6 g). Heptane (75 ml) was added and the mixture was refluxed under nitrogen for 24 h. After removal of the solvent, $W(CO)_6$ formed during the reaction was sublimed out of the residue at 40 °C. The residue was then extracted with CH_2Cl_2 and chromatographed on a 30 × 1.5 cm column packed with alumina (activity grade II) using 1:1 CH_2Cl_2–hexane as the eluent. Unreacted guaiazulene was eluted from the column first followed by compound **5** as a red-brown band. This band was concentrated and crystallization at −20 °C yielded **5** as small black crystals. The infrared spectrum of **5** in CH_2Cl_2 shows the following carbonyl bands: 2020 (s), 1942 (s), 1885 (w), 1860 (w) cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_6W_2$: C, 34.4; H, 2.5. Found: C, 34.6; H, 2.4.

Carbon-13 NMR spectra were recorded on a JEOL-100/Nicolet 1080 Fourier transform spectrometer operating at 25.036 MHz. The deuterium signal of the solvent was used for locking.

Samples of **4** and **5**, enriched to approximately 10% in ^{13}CO, were prepared by stirring a solution of each compound in CH_2Cl_2 under an atmosphere of carbon monoxide enriched to 90% in carbon-13.

The spectra of **4** were recorded in 30% acetone-d_6–70% acetone down to −89 °C. At −109 °C, 30% acetone-d_6–70% 2-methyltetrahydrofuran was used as a solvent. The spectra of **5** were recorded in 30% $CDCl_3$–70% CH_2Cl_2 down to −83 °C, and below −90 °C in 20% CD_2Cl_2, 80% $CHFCl_2$. To all of the above solvent mixtures about 5% by volume of CS_2 was added as a chemical shift standard. Tris(acetylacetonato)chromium(III), 5 mg, was added to each sample.

X-Ray Crystallography. A black crystal of **5** suitable for x-ray data collection was grown from a concentrated CH_2Cl_2 solution at −20 °C. The crystal was mounted in a glass capillary tube and sealed under argon. Preliminary x-ray examination and data collection were performed on a Syntex $P\bar{1}$ computer-controlled diffractometer equipped with a graphite-crystal monochromator in the incident beam. The crystal was found to be monoclinic and isomorphous with previously characterized[4] (gazl)$Mo_2(CO)_6$. The space group is $P2_1/n$. The widths at half-height (ω scans) of several strong reflections were less than 0.20°. Cell constants were obtained by centering on 15 strong reflections in the range $20° < 2\theta < 30°$; the cell constants and calculated volume are a = 11.767 (2) Å, b = 16.404 (3) Å, c = 10.879 (1) Å, β = 100.07 (1)°, and V = 2066.5 (5) Å^3.

The crystal used for intensity measurements was nearly spherical, with the diameter varying from 0.20 to 0.21 mm. Although the linear absorption coefficient for Mo Kα radiation is 118 cm^{-1}, the shape of the crystal ensures that the transmission coefficients, though small, will vary over only a very small range, estimated to be 0.0836–0.0940. Accordingly, absorption coefficients were neglected. Intensities were measured at 22 ± 4 °C using the θ–2θ scan method. With Mo Kα radiation, 2996 independent reflections were measured in the range $0° < 2\theta < 45°$. Scan speeds varied from 4 to 24° min^{-1}, and the scan range was from 0.8° below the Kα_1 peak to 0.8° above the Kα_2 peak.

The positional parameters reported for $(C_{15}H_{18})Mo_2(CO)_6$ were entered and allowed to refine isotropically.[5] One atom, C_{19}, had to be found by a difference Fourier map after two cycles of refinement, since its z coordinate in the Mo structure is, apparently, reported incorrectly. We find a z coordinate of 0.055 (2), whereas that given in the Mo case is 0.5836 (18). Three cycles of refinement, anisotropically on the tungsten atoms and isotropically on all other nonhydrogen atoms, gave final discrepancy indices of R_1 = 0.036 and R_2 = 0.056.

Results

(azl)$Mo_2(CO)_6$ (4). The carbon-13 NMR spectra of **4** are shown in Figure 1. The chemical shifts and line shape patterns are qualitatively the same as those previously reported[1] for **1**. Because of the similarity of the spectra, it seems safe to assume that again the fast-scrambling $Mo(CO)_3$ group is the

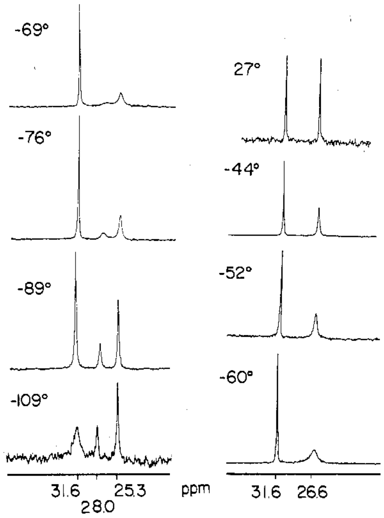

Figure 1. Carbon-13 NMR spectra of $(C_{10}H_8)Mo_2(CO)_6$ from −109 to +27 °C in the carbonyl region. Chemical shifts are measured in ppm downfield from internal CS_2.

Table I. Activation Parameters for Local Scrambling of $M(CO)_3$ groups

Compd	$\Delta\nu$, Hz	T_c, °C	E_a,[a] kcal mol^{-1}	ΔE_a,[b] kcal mol^{-1}
$(C_{10}H_8)Mo_2(CO)_6$	67.5	−60	10.5	
	c	<−109	<8.1	>2.4
$(C_{15}H_{18})Mo_2(CO)_6$	82.5	−30	11.9	
	c	<−112	<7.8	>4.1
$(C_{15}H_{18})W_2(CO)_6$	45	−30	12.3	
	252	−96	8.3	4.0

[a] Arrhenius activation energies calculated assuming a frequency factor of $10^{13.2}$. [b] The difference in activation energies between the fast and slow $M(CO)_3$ groups. [c] Frequency separations comparable to those observed for the slow $M(CO)_3$ group were assumed.

one bonded to the cyclopentadienyl portion of the azulene ligand, as in **1**.[2]

The coalescence temperatures observed for **4** compare with those for **1** as follows. First, coalescence for the fast-scrambling $Mo(CO)_3$ groups occurs at comparable temperatures (less than −109 °C for **4** and less than −112 °C for **1**). The corresponding activation energies must be essentially identical. Second, coalescence for the slow-scrambling $Mo(CO)_3$ group in **4** occurs about 30 °C lower in temperature than for the corresponding group in **1** (−60 °C for **4** and −30 °C for **1**). This corresponds to a difference in activation energies for the slow-scrambling $Mo(CO)_3$ groups in **1** and **4** of approximately 1.4 kcal mol^{-1} (see Table I).

(gazl)$W_2(CO)_6$ (5). The carbon-13 NMR spectra of **5** are shown in Figure 2. Comparison of these spectra with those for **1** allow the assignment of the fast $W(CO)_3$ group as the one bonded to the cyclopentadienyl ring. The low-temperature limiting spectrum for the fast $W(CO)_3$ group is reached at −123 °C. Solubility problems at low temperatures prevented the attainment of the limiting spectrum for **1** and **4**. The coalescence temperature of −30 °C for the slow $W(CO)_3$ group is identical with the coalescence temperature for the analogous group in the molybdenum analogue. The fast $W(CO)_3$ group coalesces nearly 20 °C higher than observed in the molybdenum analogue. Activation energies for both $W(CO)_3$ groups are about 0.5 kcal higher than those for their molybdenum analogue.

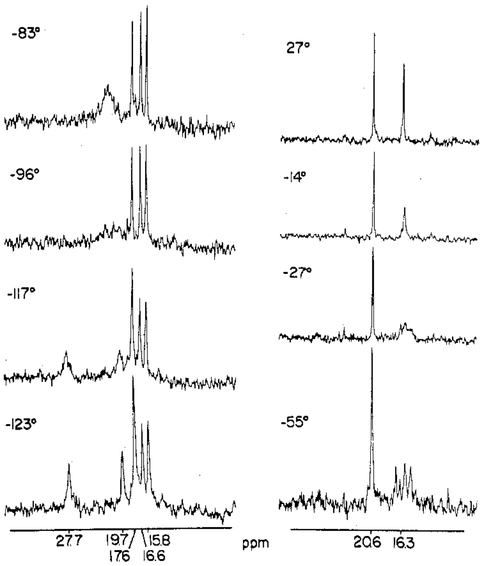

Figure 2. Carbon-13 NMR spectra of $(C_{15}H_{18})W_2(CO)_6$ from −123 to +27 °C in the carbonyl region. Chemical shifts are measured in ppm downfield from internal CS_2.

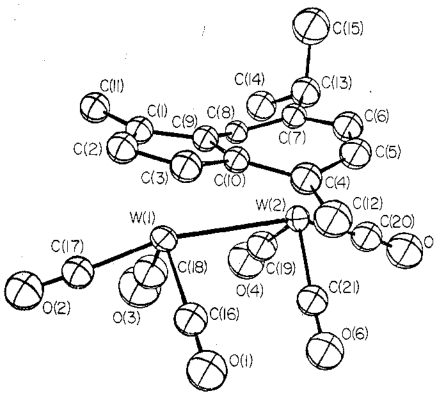

Figure 3. An ORTEP view of the molecular structure of $(C_{15}H_{18})W_2(CO)_6$. Atoms are represented by thermal vibration ellipsoids enclosing 50% of the electron density.

The W–W bond length in **5** is 3.264 (1) Å. This is identical within experimental error with the reported Mo–Mo distance in **1** of 3.267 (6) Å.[4] Other bonds, angles, and contacts in **5** are very similar to those in its molybdenum analogue.

Discussion

Comparison of the Azulene and Guaiazulene Analogues. In the case of (gazl)$Mo_2(CO)_6$, reported earlier, the considerable difference in the rates of internal scrambling for the two $Mo(CO)_3$ groups was tentatively ascribed to the different electronic effects of the cyclopentadienyl and pentadienyl groups to which they are attached. Possible steric (or electronic) effects of the methyl and isopropyl substituents on the rings were tacitly assumed to be negligible—or, at least, of secondary importance. One of our purposes in the present work was to check explicitly on this assumption.

The results now available (Table I) for compounds **1** and **4** indicate that the influence of the substituents is indeed secondary but not wholly negligible. As best one can estimate, since the slow-exchange limits were not observable in either case, the fast-scrambling $Mo(CO)_3$ groups have similar rates in **1** and **4**, but for the slow-scrambling $Mo(CO)_3$ groups, the presence of the alkyl substituents impedes scrambling. The magnitude of the effect is such that the coalescence temperature is increased by about 30 °C and the activation energy by about 1 kcal mol^{-1}. The difference in activation energies for the two different $Mo(CO)_3$ groups within the (azl)$Mo_2(CO)_6$ or (gazl)$Mo_2(CO)_6$ molecules (≥3 kcal mol^{-1}) is due mainly to the intrinsic difference between the cyclopentadienyl and pentadienyl systems but is enhanced by

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	0.225 25 (5)	0.083 66 (4)	−0.180 69 (5)	0.004 32 (4)	0.002 52 (2)	0.004 52 (5)	−0.000 26 (6)	0.001 76 (8)	−0.000 19 (6)
W(2)	0.228 69 (5)	0.215 75 (4)	0.044 39 (5)	0.004 35 (4)	0.002 16 (2)	0.004 91 (5)	−0.000 20 (6)	0.002 28 (8)	−0.000 41 (6)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
O(1)	0.196 (1)	0.2156 (7)	−0.387 (1)	4.8 (3)	C(9)	0.337 (1)	0.0641 (8)	0.018 (1)	2.3 (3)
O(2)	0.126 (1)	−0.0340 (8)	−0.398 (1)	5.0 (3)	C(10)	0.400 (1)	0.1199 (8)	−0.052 (1)	2.1 (2)
O(3)	−0.032 (2)	0.0650 (10)	−0.147 (2)	8.1 (4)	C(11)	0.277 (1)	−0.0909 (10)	−0.002 (1)	3.3 (3)
O(4)	−0.024 (1)	0.1749 (10)	0.067 (1)	6.9 (3)	C(12)	0.460 (2)	0.2572 (11)	−0.123 (2)	3.9 (3)
O(5)	0.155 (1)	0.3679 (8)	0.181 (1)	5.7 (3)	C(13)	0.288 (2)	0.1324 (10)	0.349 (2)	3.9 (4)
O(6)	0.164 (1)	0.3309 (8)	−0.184 (1)	4.8 (3)	C(14)	0.183 (2)	0.0792 (11)	0.351 (2)	4.4 (4)
C(1)	0.329 (1)	−0.0131 (9)	−0.043 (1)	2.6 (3)	C(15)	0.393 (2)	0.0952 (13)	0.437 (2)	5.9 (5)
C(2)	0.381 (1)	−0.0043 (9)	−0.151 (1)	3.0 (3)	C(16)	0.204 (1)	0.1672 (10)	−0.307 (1)	3.4 (3)
C(3)	0.427 (1)	0.0790 (9)	−0.155 (1)	2.9 (3)	C(17)	0.163 (1)	0.0124 (10)	−0.318 (1)	3.5 (3)
C(4)	0.420 (1)	0.2049 (9)	−0.025 (1)	3.0 (3)	C(18)	0.064 (2)	0.0761 (11)	−0.161 (2)	4.8 (4)
C(5)	0.427 (1)	0.2410 (9)	0.095 (1)	3.2 (3)	C(19)	0.070 (2)	0.1878 (11)	0.055 (2)	4.2 (4)
C(6)	0.386 (1)	0.2142 (9)	0.202 (1)	3.2 (3)	C(20)	0.188 (1)	0.3100 (10)	0.131 (2)	3.9 (3)
C(7)	0.323 (1)	0.1414 (9)	0.222 (1)	2.5 (3)	C(21)	0.187 (1)	0.2864 (9)	−0.102 (1)	3.4 (3)
C(8)	0.286 (1)	0.0852 (8)	0.128 (1)	2.1 (3)					

[a] The form of the anisotropic thermal parameter is $\exp[-\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table III. Intramolecular Distances (Å)

(i) Distances from Tungsten Atoms			
W(1)-W(2)	3.264 (1)	W(2)-C(4)	2.500 (14)
-C(1)	2.370 (13)	-C(5)	2.340 (15)
-C(2)	2.310 (14)	-C(6)	2.294 (14)
-C(3)	2.341 (14)	-C(7)	2.387 (13)
-C(9)	2.344 (12)	-C(8)	2.377 (12)
-C(10)	2.349 (12)	-C(19)	1.943 (17)
-C(16)	1.929 (15)	-C(20)	1.916 (16)
-C(17)	1.934 (15)	-C(21)	1.964 (15)
-C(18)	1.947 (20)		
(ii) Distances within the Bicyclic Ring System			
C(1)-C(2)	1.420 (18)	C(5)-C(6)	1.409 (19)
C(2)-C(3)	1.473 (19)	C(6)-C(7)	1.438 (19)
C(3)-C(10)	1.387 (18)	C(7)-C(8)	1.389 (17)
C(10)-C(9)	1.472 (17)	C(8)-C(9)	1.472 (17)
C(9)-C(1)	1.423 (18)	C(10)-C(4)	1.438 (18)
C(4)-C(5)	1.422 (19)		
(iii) Other Distances in the Guaiazulene Ligand			
C(1)-C(11)	1.516 (19)	C(13)-C(14)	1.524 (23)
C(4)-C(12)	1.514 (20)	C(13)-C(15)	1.549 (25)
C(7)-C(13)	1.513 (20)		
(iv) Carbon-Oxygen Distances			
C(16)-O(1)	1.167 (16)	C(19)-O(4)	1.157 (19)
C(17)-O(2)	1.182 (17)	C(20)-O(5)	1.191 (18)
C(18)-O(3)	1.183 (23)	C(21)-O(6)	1.143 (16)
(v) Distances between the Guaiazulene Ligand and the Carbonyl Ligands			
C(16)-C(3)	3.196 (20)	C(19)-C(14)	3.712 (23)
C(17)-C(3)	3.468 (21)	C(20)-C(7)	3.254 (20)
C(17)-C(2)	2.882 (20)	C(20)-C(6)	2.802 (21)
C(17)-C(1)	3.298 (20)	C(20)-C(5)	3.118 (22)
C(18)-C(1)	3.479 (23)	C(20)-C(13)	3.810 (22)
C(19)-C(8)	3.032 (20)	C(21)-C(4)	3.035 (21)
C(19)-C(7)	3.287 (21)	C(21)-C(12)	3.296 (21)
C(19)-C(13)	3.839 (22)		

Table IV. Bond Angles (deg)

(i) Around the Tungsten Atoms			
W(2)-W(1)-C(16)	92.7 (4)	W(1)-W(2)-C(19)	90.2 (5)
-C(17)	158.8 (5)	-C(20)	159.1 (5)
-C(18)	81.1 (5)	-C(21)	79.3 (4)
C(16)-W(1)-C(17)	83.9 (6)	C(19)-W(2)-C(20)	80.6 (7)
-C(18)	96.6 (7)	-C(21)	94.8 (7)
C(17)-W(1)-C(18)	78.6 (7)	C(20)-W(2)-C(21)	82.9 (6)
(ii) Within the Carbonyl Ligands			
W(1)-C(16)-O(1)	175.9 (1.3)	W(2)-C(19)-O(4)	175.6 (1.5)
-C(17)-O(2)	177.1 (1.3)	-C(20)-O(5)	175.0 (1.4)
-C(18)-O(3)	174.6 (1.7)	-C(21)-O(6)	176.4 (1.3)
(iii) Within the Azulene Nucleus			
C(2)-C(1)-C(9)	106.9 (1.1)	C(4)-C(10)-C(9)	125.0 (1.2)
C(1)-C(2)-C(3)	109.5 (1.2)	C(8)-C(9)-C(10)	126.0 (1.1)
C(2)-C(3)-C(10)	106.6 (1.2)	C(7)-C(8)-C(9)	129.6 (1.2)
C(3)-C(10)-C(9)	108.9 (1.1)	C(6)-C(7)-C(8)	123.0 (1.2)
C(1)-C(9)-C(10)	108.1 (1.1)	C(5)-C(6)-C(7)	129.9 (1.3)
C(1)-C(9)-C(8)	125.8 (1.2)	C(4)-C(5)-C(6)	130.9 (1.4)
C(3)-C(10)-C(4)	125.9 (1.2)	C(5)-C(4)-C(10)	125.3 (1.2)
(iv) For Substituents on Azulene			
C(2)-C(1)-C(11)	125.8 (1.2)	C(8)-C(7)-C(13)	120.5 (1.2)
C(9)-C(1)-C(11)	127.3 (1.2)	C(7)-C(13)-C(14)	114.9 (1.3)
C(10)-C(4)-C(12)	117.4 (1.2)	C(7)-C(13)-C(15)	106.9 (1.3)
C(5)-C(4)-C(12)	116.1 (1.3)	C(14)-C(13)-C(15)	109.3 (1.3)
C(6)-C(7)-C(13)	116.3 (1.2)		

approximately an additional 1 kcal mol^{-1} by the presence of the alkyl substituents in the guaiazulene compound.

Whether the small enhancement caused by the alkyl substituents has a steric or an electronic (inductive) origin is impossible to say with certainty. The crystallographic structural results for **1**[4] and its isomorphous tungsten analogue appear to provide a prima facie case against a steric origin. All carbonyl to alkyl distances are much longer (Table III) than carbonyl to ring distances. However, in solution, the isopropyl group will be free to rotate, and this barrier is likely to be lower[8] than that for the slower Mo(CO)$_3$ scrambling process. Thus, the mean or time-average distances from carbonyl groups to isopropyl carbon atoms may be shorter in solution than in the crystal. We estimate from the crystallographic data that the effective contact distance could be as short as 2.6 Å; clearly, this might be able to account for the increase of about 1 kcal mol^{-1} in activation energy on introducing the isopropyl groups.

Although inductive effects of alkyl substituents on carbonyl scrambling in molecules of this type have never been demonstrated, it is clear from comparing the CO stretching frequencies in groups of molecules such as $(C_5H_5)_2Mo_2(CO)_6$ and $(C_5Me_5)_2Mo_2(CO)_6$[9] and (azl)Mo$_2$(CO)$_6$, (gazl)Mo$_2$(CO)$_6$, and (4,6,8-Me$_3$azl)Mo$_2$(CO)$_6$[3] that there do exist inductive effects that are evidenced by lower CO stretching frequencies in the substituted molecules. It is conceivable that these could influence the dynamics as well, although this is purely speculative.

Comparison of the Molybdenum and Tungsten Analogues. The main reason for carrying out the crystallographic study of the (gazl)W$_2$(CO)$_6$ compound **5** was to see if there were any structural explanation for the one difference (but a very conspicuous one) between the ^{13}C NMR spectra of **1** and **5**, namely, the appearance of only two lines (in a 2:1 intensity ratio) for the slow-scrambling Mo(CO)$_3$ group but three lines for the corresponding W(CO)$_3$ group. In both cases, the unsymmetrical set of ring substituents in **1** and **5** destroys the mirror plane that exists in **4**, so that, in principle, both **1** and **5** ought to display three separate lines for this $M(CO)_3$ group. The lack of any qualitative difference or any significant quantitative difference in the structures of **1** and **5** leaves us at a loss to explain the observations. Evidently, a very subtle effect is involved.

The change from Mo to W in going from **1** and **5** has essentially no effect on the ease of the carbonyl scrambling processes in this case. This is not particularly surprising, but at the same time, no valid generalization can be based on this one case.

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Registry No. **1**, 12320-70-6; **4**, 60295-03-6; **5**, 60306-24-3; $(CH_3CN)_3W(CO)_3$, 16800-47-8; ^{13}C, 14762-74-4.

Supplementary Material Available: Listing of structure factor amplitudes (10 pages). Ordering information is given on current masthead page.

References and Notes

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Effects of $M^{III}_2TeO_6$ Substitutions on the Crystal Structure and Transition Temperature of VO_2

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The $V_{1-x}M^{III}_{2x/3}Te_{x/3}O_2$, where M = Fe, Cr, or Al, series of solid solutions have been prepared and studied by x-ray diffraction and DTA methods. It has been shown that all the substitutions are partial. Further, the phase transition sequences $M_1 \rightarrow M_2 \rightarrow M_4$ for $V_{1-x}M^{III}_{2x/3}Te_{x/3}O_2$, M = Fe or Cr, and $M_1 \rightarrow M_2$ for $V_{1-x}Al_{2x/3}Te_{x/3}O_2$ have been examined at the VO_2 end. It is interesting to report that the T_{tr} shifts toward higher temperatures with increasing amounts of $M^{III}_2TeO_6$ in all the systems.

Introduction

The system VO_2–$M^{III}_2M^{VI}O_6$ has been the subject of several investigations in recent years. Bernier and Poix[1] were first to recognize the trirutile V_2WO_6 solid solution in the VO_2–WO_2 system and soon after Bernigaud, Bernier, and Michel[2] reported that V_2WO_6 dissolves in all proportions in VO_2. Further it has been shown that the rutile structure exists over a large composition range and the T_{tr} shifts toward lower temperatures. More recently Neurgaonkar and Roy[3] showed that complete solid solution also exists between VO_2 and Cr_2WO_6 and demonstrated the existence of the monoclinic (M_2) and the rutile (R) structures, at room temperature, as a function of composition. They also reported that the T_{tr} first decreased and then increased with increasing amounts of Cr_2WO_6 in VO_2. These results suggest that the T_{tr} should shift toward a higher temperature, if both W^{6+} and V^{3+} are replaced by the smaller cations. The present investigation has been undertaken to study the effects of replacing V_2WO_6 by $M^{III}_2TeO_6$, where M = Fe, Cr, or Al, on solid solubility, on structural changes, and finally on the transition temperature.

Experimental Section

The starting materials used were V_2O_5 (Research Organic/Inorganic Chemical Corp.), TeO_2 (Johnson Mathey Chemical), Cr_2O_3, Al_2O_3, and Fe_2O_3 (Fischer Scientific Co.). V_2O_3 was prepared by hydrogen reduction of V_2O_5 at 800 °C for 8–10 h. $M^{III}_2TeO_6$ phases were first prepared at 750 °C and then samples were weighed by mixing the appropriate amounts of V_2O_5, V_2O_3, and $M^{III}_2TeO_6$. Detailed experimental techniques have been described elsewhere.[3] The reaction temperature was raised 100 °C/day and kept at 750–800 °C for 2–8 days, after which the samples were quenched and analyzed.

Table I. Synthesis Conditions and Phase Analyses for $V_{1-x}M_{2x/3}Te_{x/3}O_2$ Systems

System	Compn	Reacn temp, °C	Structure[a]
$V_{1-x}Al_{2x/3}$-$Te_{x/3}O_2$	$0 \leqslant x \leqslant 0.01$	760 °C/8 days	M_1
	$0.012 \leqslant x \leqslant 0.12$	760 °C/8 days	M_2
	$0.13 \leqslant x \leqslant 0.69$	760 °C/8 days	$M_2 + T_R$
	$0.70 \leqslant x \leqslant 1.0$	760 °C/8 days	T_R
$V_{1-x}Cr_{2x/3}$-$Te_{x/3}O_2$	$0 \leqslant x \leqslant 0.01$	800 °C/8 days	M_1
	$0.015 \leqslant x \leqslant 0.08$	800 °C/8 days	M_2
	$0.09 \leqslant x \leqslant 0.21$	800 °C/8 days	M_4
	$0.22 \leqslant x \leqslant 0.69$	750 °C/8 days	$M_2 + Cr_2O_3$
	$0.70 \leqslant x \leqslant 1.0$	750 °C/8 days	T_R
$V_{1-x}Fe_{2x/3}$-$Te_{x/3}O_2$	$0 \leqslant x \leqslant 0.01$	760 °C/2 days	M_1
	$0.015 \leqslant x \leqslant 0.08$	760 °C/2 days	M_2
	$0.09 \leqslant x \leqslant 0.30$	760 °C/2 days	M_4
	$0.31 \leqslant x \leqslant 0.64$	750 °C/2 days	Unknown
	$0.65 \leqslant x \leqslant 1.0$	750 °C/2 days	T_R

[a] M_1 = monoclinic; M_2 = monoclinic; M_4 = monoclinic; T_R = trirutile.

Room- and high-temperature x-ray powder data were obtained by using a Picker diffractometer with nickel-filtered Cu Kα radiation. For phase identification a scanning speed of 1° in 2θ/min was used.

Results and Discussion

Synthesis of $V_{1-x}M^{III}_{2x/3}Te_{x/3}O_2$. The phase $V_{1-x}M^{III}_{2x/3}Te_{x/3}O_2$, where M = Fe, Cr, or Al, has been prepared by substituting M_2TeO_6 (trirutile) for VO_2 as in

$$(1-x)VO_2 + (x/3)M_2TeO_6 \rightarrow V_{1-x}M^{III}_{2x/3}Te_{x/3}O_2$$

Table I summarizes the synthesis conditions and phase analyses for the different phases which have been prepared