metal carbonyl $MnRe(CO)_{10}$ five intense absorptions in the carbonyl stretching region of the infrared spectrum (2064 (m), 2039 (m), 2006 (s), 1974 (m), and 1968 (m) cm^{-1}; CCl_4 solution). While it is true that the strict application of symmetry rules requires that there be six infrared-active fundamental modes for this carbonyl, in fact we[2a] and others[2b] had earlier observed that it exhibits only three principal absorptions (2054 (m), 2017 (s), and 1978 (m) cm^{-1}; cyclohexane solution) which resemble those of the symmetrical dimetal decacarbonyls. Whatever differences may arise concerning the assignment of the modes, however, it is apparent that there must be some additional problem if two groups of workers report a different number of bands for the same species. A similar discrepancy was brought to our attention recently when we had occasion to record the spectrum of $(C_5H_5)(CO)_3WMn(CO)_5$, for which we obtained in cyclohexane solution fewer principal absorptions (2088 (m), 2028 (w), 1996 (s), 1979 (s), 1915 (w), and 1899 (m) cm^{-1}) than reported[1] by Nesmeyanov, *et al.*, in carbon tetrachloride solution (2081 (m), 2049 (m), 2021 (w), 1988 (s), 1971 (s), 1905 (w), and 1888 (m) cm^{-1}). In both this case and that for $MnRe(CO)_{10}$ our suspicions were aroused that the differences might be due to chemical impurities arising from reaction with solvent. One of us had earlier noted during spectroscopic studies that $Mn_2(CO)_{10}$ reacts with carbon tetrachloride under mild conditions.[3]

Dealing first with the case of $(C_5H_5)(CO)_3WMn(CO)_5$, we note that an infrared spectrum of the complex in carbon tetrachloride, recorded as quickly as possible after preparation of the solution, does indeed show one additional band (2055 cm^{-1}) over that noted in cyclohexane solution. We observe, in addition, that this band continues to grow rapidly, until it becomes apparent that it is one of the strong bands of $Mn(CO)_5Cl$, the other of which (2000 cm^{-1}) is initially obscured by a genuine absorption of $(C_5H_5)(CO)_3WMn(CO)_5$. After 3 hr the entire sample is converted to a mixture of $Mn(CO)_5Cl$ and its decomposition product $[Mn(CO)_4Cl]_2$.[3] No attempt was made to determine the fate of the tungsten and no $(C_5H_5)(CO)_3WCl$ or other soluble carbonyl-containing species was observed. The rhenium analogs $(C_5H_5)(CO)_3MRe(CO)_5$ (M = Mo, W) are apparently more resistant, and in carbon tetrachloride a pattern of six carbonyl bands is reported[1] similar to that observed by us for $(C_5H_5)(CO)_3WMn(CO)_5$ in cyclohexane.

In the case of $MnRe(CO)_{10}$ the discrepancy arises from a different source; this carbonyl does *not* react with carbon tetrachloride even within 24 hr. The sample used to record the spectrum reported by Nesmeyanov, *et al.*,[1] is perfectly fitted by a mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ both in our laboratory and also by taking the peaks reported in that paper for these derivatives. As we have formerly reported,[2] the published[4] synthesis of $MnRe(CO)_{10}$ leads to a product mixed with some of the symmetrical dimetal decacarbonyls. In fact, from the combination of $NaRe(CO)_5$ and $Mn(CO)_5Br$ we obtain principally a mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. A high yield of $MnRe(CO)_{10}$ with only traces of the symmetrical decacarbonyls is obtained from $NaMn(CO)_5$ and $Re(CO)_5Br$.

One last point needs to be made concerning a footnote in the paper by Nesmeyanov, *et al.*, namely:[1] "Weak bands in the 1800–2100 cm^{-1} region, which have intensities 1–2 orders lower than the intensities of ν_{CO} cannot be assigned to fundamental vibrations, and are not considered further." This is a misleading assumption. It has already been demonstrated in the case of the pentacarbonyl halides[5] and hydrides[6] of Mn, Tc, and Re that a fundamental mode can be quite weak and this is undoubtedly also true for $MnRe(CO)_{10}$. Following the study of the Raman spectrum of $Re_2(CO)_{10}$ by Cotton and Wing,[7] we can now assign the weak band of $MnRe(CO)_{10}$ at 2124 cm^{-1} (band E in Figure 1 of ref 2a) as the A_1 mode, which has only weakly gained infrared activity compared to that of the corresponding A_1 mode of the symmetrical decacarbonyls, which is strictly only Raman active. This is no doubt the result of only a small departure from D_{4d} to C_{4v} symmetry for the *effective* electron density available to the ten terminal carbonyls from the dimetal core in going from $M_2(CO)_{10}$ to $MM'(CO)_{10}$.

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The Presence of $H_5O_2^+$ in Erbium and Yttrium Oxalate–"Hydrogen Oxalate" Trihydrate[1]

Sir:

The X-ray crystal structure of $Er(C_2O_4)(HC_2O_4)\cdot 3H_2O$ was recently reported by Steinfink and Brunton.[2] These authors undertook the study because the compound was thought to contain both the anion $C_2O_4^{2-}$ and the acid anion $HC_2O_4^-$. They found the space group to be $P_{4/n}$ with two molecules per unit cell and interpreted their results in terms of a disorder between the oxalate and the acid oxalate ions. The six waters occupy two crystallographically distinct positions in the cell. Two of the waters are in the twofold positions 2c and each occupies one of the nine coordination positions about the erbium. The remaining four waters caused some difficulty, being statistically distributed among the eightfold positions 8g, and had very short O–O distances. The two shortest distances between these disordered water oxygens were observed to be 2.43 and 1.87 Å.[2]

We wish to point out that the thermal ellipsoids for the oxalate oxygens are normal for a completely ordered oxalate ion and show no elongation along the C–O bond as one might expect for a disorder between

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TABLE I

FRACTIONAL COORDINATES AND THERMAL PARAMETERS ($\times 10^4$) FOR $H_5O_2^+Y(C_2O_4)_2^- \cdot H_2O$

	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Y	7500	2500	2884.2 (4)	32.6 (26)	30.5 (25)	20.9 (3)	17.5 (46)	0	0
C_1	355 (11)	232 (13)	8001 (9)	1.7 (2)[b]					
C_2	421 (10)	251 (11)	3021 (8)	1.1 (2)[b]					
O_1	6255 (6)	296 (7)	3521 (5)	61 (9)	67 (9)	31 (6)	−21 (15)	−48 (11)	28 (11)
O_2	6326 (6)	200 (7)	8519 (5)	57 (9)	53 (8)	31 (6)	−61 (14)	−21 (10)	19 (10)
O_3	5431 (6)	1593 (7)	6760 (5)	44 (9)	61 (11)	37 (6)	−33 (16)	−34 (11)	10 (12)
O_4	5484 (6)	1609 (7)	1736 (5)	62 (10)	38 (10)	25 (5)	−22 (16)	−4 (11)	21 (11)
O_5 (H_2O)[c]	7500	2500	4804 (3)	55 (12)	95 (14)	22 (3)	4 (29)	0	0
O_6 ($H_5O_2^+$)[d]	6188 (4)	7012 (4)	4724 (3)	101 (5)	146 (6)	34 (3)	17 (10)	5 (7)	43 (7)

[a] Coefficients in the temperature factor; $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Constrained to be isotropic. [c] O_5 is the H_2O which caps the antiprism of oxalate oxygen around Y^{3+}. [d] O_6 is one of a pair of oxygens in the $H_5O_2^+$ ion, separated by 2.434 (8) Å.

C–O and C–OH bonds. Of special importance, the H_2O–OH_2 distance of 2.43 Å is strongly suggestive of the well-established $H_5O_2^+$ ion.[3–13] In view of these facts it is reasonable to propose that the acid hydrogen is not connected to the carbonyl oxygen but is actually on (or very near) the twofold axis between the two water oxygen positions having an interatomic distance of 2.43 Å. The hydrogen positions have the same occupancy number as the oxygen positions that they connect.

We prepared both the erbium and the yttrium compounds in the manner described by Steinfink and Brunton.[2] Heavy metal and carbon–hydrogen analyses confirmed their formula. We indeed find their disordered phase for the Er compound (a_0 = 8.67 Å, c_0 = 6.42 Å) but more frequently find in the same preparation a phase with the same a axis but with a *doubled c* axis. Our single phase for the yttrium compound, which is said to be isostructural to the erbium compound,[2] invariably has the *doubled c* axis. The space group for the doubled cell is $P4_{2/n}$ (instead of $P_{4/n}$). In this doubled cell one can readily place a completely ordered structure having $H_5O_2^+$ groups. In so doing, the "short" 2.43-Å oxygen–oxygen distance between the two water molecules now arises naturally from the $H_5O_2^+$ ion, the troublesome 1.87-Å O–O distance no longer is present, and the oxalate coordination of X^{3+} is normal.

To verify our proposed structure, intensity data were collected to θ = 60° in the usual manner[14] on a single crystal of "$Y(C_2O_4)(HC_2O_4) \cdot 3H_2O$" ($\mu$ = 63 cm^{-1}). Unit cell constants were found to be a_0 = 8.697 (7) and c_0 = 12.832 (10) Å. Used was a computer-controlled Picker four-circle goniostat with Mo Kα radiation.

Least-squares calculations were made on all data (1487 reflections were measured, of which 710 were observed). The function minimized was $\Sigma w_i^2(F_o^2 - F_c^{*2})^2$ where F_c^* is defined in ref 14. Because of the approximate translational symmetry of $c/2$ for all light atoms except the two oxygens in the $H_5O_2^+$ ion, refinement of anisotropic thermal parameters for the two oxalate carbon atoms was not possible. The refined structure gave $R = 0.112 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for all observed reflections. The R index calculated for observed reflections having even l values only was R = 0.032; for odd l values only the R index was 10 times greater (0.31). The atomic parameters are summarized in Table I. Interatomic distances essentially agree with those of ref 2 and are not repeated here. The exceptions are the O–O distance of 1.87 Å which is, of course, not present in the doubled cell and the interpretation of the origin of the 2.43-Å spacing between the two water oxygens. The geometry of the $H_5O_2^+$ ion can be inferred from the O–O contacts with the oxalate oxygens it links. The ion is in the trans conformation as is frequently found for it. See Figure 1. We do not propose to undertake a neutron-diffraction study.

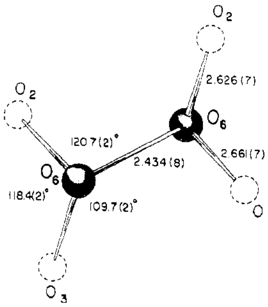

Figure 1.—Distances and angles from $H_5O_2^+$ (O_6–O_6) to oxalate oxygens (O_2, O_3).

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