

Combination Spectra: Structure and Bonding in Tetrakis(tricarbonyl-organothiomanganese and -rhenium) Compounds

By P. S. Braterman, Department of Chemistry, University of Glasgow, Glasgow W.2

Species of the type $[M(CO)_3SR]_x$ ($M = Mn, Re$) are shown from fundamental and combination infrared spectra to be tetrameric in solution, and to have a regular tetrahedral structure with no metal-metal bonding

COMBINATION spectra have been used in investigations of metal-metal bonding,¹⁻⁵ anharmonicity,^{6,7} and the structure of binuclear complexes of known molecular formula.^{4,5,8} The present work establishes the molecular formula and structure, and the main features of the bonding, in the polymeric materials of formula $[M(CO)_3SR]_x$ ($M = Mn$ or Re).

The reaction of $M(CO)_5Br$ with thiols gives rise to products $(CO)_4M(SR)_2M(CO)_4$,⁹ which lose a further molecule of carbon monoxide from each metal to give the final products $[M(CO)_3SR]_x$.¹⁰⁻¹² These materials were originally formulated as trimeric, but later work, including mass-spectroscopic studies, supported a tetrameric structure, at least for the Mn compounds in the vapour phase.¹² The extreme simplicity of the reported infrared spectrum in the $\nu(CO)$ fundamental region^{10,11}

were measured on a Perkin-Elmer 225 spectrophotometer, both in cyclohexane and in carbon tetrachloride. Combination spectra (CCl_4 , 1 cm. path length) were measured on a Unicam SP 700C calibrated against atmospheric water,¹³ and on a Beckman DK 2-A calibrated using indene¹³ and 1,2,4-trichlorobenzene.¹⁴ Each spectrum was calibrated at both high- and low-energy ends. Spectra obtained on the two instruments agreed to within ± 2 cm.⁻¹. The spectrum of a fresh solution was unchanged after 24 hr., and showed no bands attributable to $M(CO)_5Cl$. We therefore discount the possibility of decomposition, which may¹⁵ have interfered with previous studies, in particular of $[C_5H_5Fe(CO)_2]_2$.^{4,8}

RESULTS AND DISCUSSION

All three compounds show two strong bands in the $\nu(CO)$ region, with weak shoulders (¹³CO satellites)

TABLE I
Infrared spectra and $\nu(CO)$ frequencies

Substance	Fundamentals (cyclohexane)	Fundamentals (CCl_4)	Overtones (CCl_4)	Fundamental frequencies (CCl_4)
$[Mn(CO)_3SEt]_4$	2017 [$T_2(1)$]; 2008w (¹³ CO); 1944 [$T_2(2)$]; 1937w,sh (¹³ CO)	2016 [$T_2(1)$]; 2007w (¹³ CO); 1942 [$T_2(2)$]; ~1925w,sh (¹³ CO)	4060 [$A_1 + T_2(1)$]; 4030 [$2T_2(1)$]; 4010w (¹³ CO); 3986 [$A_1 + T_2(2)$]; 3958 [$T_2(1) + T_2(2)$]; 3935 [$T_1 + T_2(1)$]; 3896 [$E + T_2(2)$]; 3886 [$2T_2(2)$]; 3865 [$T_1 + T_2(2)$]; 3846 [$2T_1(1)$]	A_1 2044 $T_2(1)$ 2016 E 1954 $T_2(2)$ 1942 T_1 1923
$[Mn(CO)_3S-p\text{-tolyl}]_4$	2023 [$T_2(1)$]; 2013w,sh (¹³ CO); 1949 [$T_2(2)$]; ~1935w,sh (¹³ CO)	2022 [$T_2(1)$]; 2012w,sh (¹³ CO); 1948 [$T_2(2)$]; ~1930w,sh (¹³ CO)	4071 [$A_1 + T_2(1)$]; 4045 [$2T_2(1)$]; 3999 [$A_1 + T_2(2)$]; 3972 [$T_2(1) + T_2(2)$]; 3953 [$T_1 + T_2(1)$]; 3912 [$E + T_2(2)$]; 3900 [$2T_2(2)$]; 3882 [$T_1 + T_2(2)$]; 3866 ($2T_1$)	A_1 2049 $T_2(1)$ 2022 E 1963 $T_2(2)$ 1949 T_1 1933
$[Re(CO)_3SPh]_4$	2030 [$T_2(1)$]; 2020w (¹³ CO); 1946 [$T_2(2)$]; ~1930w,sh (¹³ CO)	2030 [$T_2(1)$]; 2020w,sh (¹³ CO); 1944 [$T_2(2)$]; ~1925w,sh (¹³ CO)	4082 [$A_1 + T_2(1)$]; 4060 [$2T_2(1)$]; 3998 [$A_1 + T_2(2)$]; 3974 [$T_2(1) + T_2(2)$]; 3956 [$T_1 + T_2(1)$]; 3898 [$E + T_2(2)$]; 3889 [$2T_2(2)$]; 3874 [$T_1 + T_2(2)$]; 3858 ($2T_1$)	A_1 2052 $T_2(1)$ 2030 E 1954 $T_2(2)$ 1944 T_1 1929

led us to think that combination spectra could be of use both in assigning a symmetry (and hence a stoichiometry), and in elucidating the bonding.

EXPERIMENTAL

$[Mn(CO)_3SEt]_x$, $[Mn(CO)_3S-p\text{-tolyl}]_x$, and $[Re(CO)_3SPh]_x$ were donated by Dr. E. W. Abel. Fundamental spectra

¹ J. Lewis, A. R. Manning, J. R. Miller, M. J. Ware, and P. Nyman, *Nature*, 1965, **207**, 142.

² F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 1328.
³ J. M. Smith, Ph.D., U.C.L.A., 1966 (*Diss. Abs.*, 1967, 2968A).

⁴ P. S. Braterman and D. T. Thompson, *J. Organometallic Chem.*, 1967, **10**, P11.

⁵ P. S. Braterman and D. T. Thompson, *J. Chem. Soc. (A)*, 1968, 1454.

⁶ J. M. Smith and L. H. Jones, *J. Mol. Spectroscopy*, 1966, **20**, 248.

⁷ F. A. Cotton, A. Musco, and G. Yagupsky, *Inorg. Chem.*, 1967, **7**, 1357.

⁸ F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, 1967, **7**, 15.

at slightly lower frequency. This suggests that the molecule as a whole is highly symmetrical. The spectrum is consistent with a structure in which all $M(CO)_3$ units are in equivalent environments of C_3 symmetry; small deviations from this symmetry are known, at least in single-nucleus species,¹⁶ to give rise to three well

⁹ W. Hieber and W. Schropp, *Z. Naturforsch.*, 1959, **14b**, 460.

¹⁰ E. W. Abel, B. C. Crosse, and D. B. Brady, *J. Amer. Chem. Soc.*, 1965, **87**, 4397; E. W. Abel and B. C. Crosse, *J. Chem. Soc. (A)*, 1966, 1141.

¹¹ A. G. Osborne and F. G. A. Stone, *Chem. Comm.*, 1965, 361; *J. Chem. Soc. (A)*, 1966, 1143.

¹² M. Ahmad, G. R. Knox, F. J. Preston, and R. I. Reed, *Chem. Comm.*, 1967, 138.

¹³ Tables of Wavenumbers for the Calibration of Infrared Spectrometers, I.U.P.A.C., London, 1961.

¹⁴ E. K. Plyler, L. R. Baine, and M. Noack, *J. Res. Nat. Bur. Stand.*, 1957, **58**, 195.

¹⁵ A. R. Manning, personal communication.

¹⁶ A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 1962, 4715.

resolved active bands. The high intensity of the ^{13}CO bands, and their comparative closeness to the main bands, suggest motions including many CO groups.

The only structure in which all $\text{M}(\text{CO})_3$ groups are equivalent and symmetrical, and in which the spectrum can show an inactive fundamental with an active overtone, is a regular tetrahedron $[\text{M}(\text{CO})_3\text{SR}]_4$. The logical possibility that the simplicity of the fundamental spectrum is due to accidental degeneracy is incompatible with the observed richness of the combination spectrum. The combination spectrum is therefore assigned in T_d symmetry using the table of symmetry modes and combination bands derived by standard methods and presented in Table 2.

TABLE 2

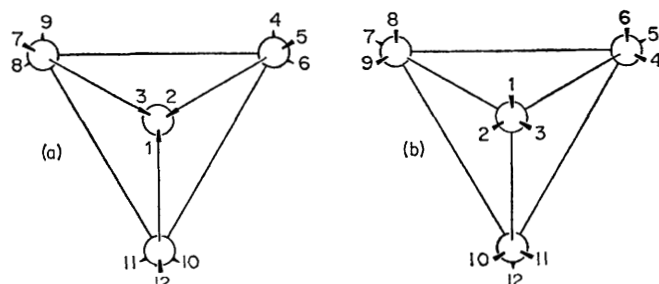
I.r.-active fundamentals and binary combinations of $[\text{M}(\text{CO})_3\text{SR}]_4$ (T_d)				
	A_1	$T_2(1)$	E	T_1
Fundamental		p, f		
$+A_1$		p, f		
$+T_2(1)$		p, f	p	p, f
$+E$			p, f	p
$+T_2(2)$			p, f	p, f
$+T_1$				p, f

p = Predicted; f = found.

The A_1 mode [derived from the symmetrical a_1 vibration of the $\text{M}(\text{CO})_3$ groups] is expected at higher frequency on general grounds,⁴ and, of the two remaining i.r.-inactive modes, T_1 is distinguished from E by the activity of its overtone. The T_1 mode, being both Raman- and i.r.-inactive, could not have been detected in solution except from combination spectra.

The only ambiguity of assignment concerns the band listed as $(T_2(2) + E)$. Since no other combinations containing E are found [though with hindsight it is possible to see weak shoulders near the predicted values of $(T_2(1) + E)$], the assignments $(T_2(1) + E)$ and $(T_1 + E)$ are logically possible. However, inspection of equation (1) shows that E is expected at higher frequency than T_1 , but at a frequency not much, if at all, higher than $T_2(2)$. The only reasonable assignment is, therefore, the one adopted.

There are two possible molecular geometries (Figure) that satisfy the requirement of T_d geometry. The secular equations [neglecting interaction of $\nu(\text{CO})$ and other modes] are given in (1).



Possible structures of $[\text{M}(\text{CO})_3\text{SR}]_4$; S atoms are omitted for clarity, and lines represent spatial relations and do not imply bonds

$$K = k_{11}, k_i = k_{12}, a = k_{16}, b = k_{1,12}, c = k_{14}, d = k_{15}$$

$$A_1: K + 2k_i + 2a + b + 2c + 4d - 4.0383 \times 10^{-6} \nu^2 = 0$$

$$E: K - k_i - a + b + 2c - 2d - 4.0383 \times 10^{-6} \nu^2 = 0$$

$$T_1: K - k_i - a - b + 2d - 4.0383 \times 10^{-6} \nu^2 = 0$$

$$T_2: \begin{vmatrix} P & Q \\ Q & R \end{vmatrix} = 0$$

where

$$P = K + 2k_i - (2/3)a - (1/3)b - (2/3)c - (4/3)d - 4.0383 \times 10^{-6} \nu^2$$

$$Q = (\sqrt{2/3})(2a - 2b + 2c - 2d)$$

$$R = K - k_i + (5/3)a + (1/3)b - (4/3)c - (2/3)d - 4.0383 \times 10^{-6} \nu^2 \quad (1)$$

The force constant K can be found unambiguously, leaving five interaction constants to be found from only four independent equations.

Of the five, k_i is expected *a priori* to be non-negligible. The problem was solved by setting each of a, b, c , and d in turn equal to zero; in each case d was very small (0.03 mdyne/\AA or less), and we therefore take the set of force constants calculated assuming $d = 0$. [Because of the quadratic form of equation (1), an alternative solution is formally possible; in it the values of a and k_i are interchanged, to give the physically unacceptable result $k_i < 0.1$]. The results are in Table 3; we also

TABLE 3

Force constants of $[\text{M}(\text{CO})_3\text{SR}]_4$ and related species ^a

	K	k_i	a	b	c	d^b
$[\text{Mn}(\text{CO})_3\text{SEt}]_4$	15.62	0.46	0.07	0.12	0.06	[0]
$[\text{Mn}(\text{CO})_3\text{S-}p\text{-tolyl}]_4$	15.72	0.44	0.03	0.24	0.03	[0]
$[\text{Re}(\text{CO})_3\text{SPh}]_4$	15.72	0.50	0.02	0.16	0.03	[0]
$\text{Mn}(\text{CO})_3\text{DS}\cdot\text{Br}^c$	15.81 ^d					
$\text{Mn}(\text{CO})_3\text{DA}\cdot\text{I}^c$	15.55 ^d					
$\text{Mn}(\text{CO})_3\pi(\text{C}_6\text{H}_5)^e$	15.47	0.55				
$\text{Re}(\text{CO})_3\pi(\text{C}_6\text{H}_5)^e$	15.33	0.57				

^a In CCl_4 ; from data of Table 1. ^b Assumed zero. ^c In CHCl_3 , from data of ref. 16; DS = $\text{PhS}\cdot\text{C}_6\text{H}_4\cdot\text{SPh}$; DA = $o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$. ^d Mean force constant, from equation (2). ^e Data from R. L. Pruett and E. L. Morehouse, *Chem. and Ind.*, 1958, 980.

give the average force constant of several species of

$$\bar{K} = 4.0383 \times 10^{-6} \sum_i g_i \nu_i^2 / \sum_i g_i \quad (2)$$

type $\text{Mn}(\text{CO})_3\text{L}_2\text{X}$. [In equation (2), g_i is the degeneracy and ν_i the frequency of the i th $\nu(\text{CO})$ mode].

Structural Conclusions; Nature of Bonding.—The force constant K for the CO stretch of the manganese compounds is typical of the average value in the $\text{Mn}^{\text{I}}(\text{CO})_3$ grouping. The smallness of the interaction constants between CO groups on different metals indicates that there is little or no metal-metal bonding; this result is implicit in the small separation between A_1 and $T_2(1)$ [compare the separation of 55 cm^{-1} in $\text{Mn}_2(\text{CO})_{10}$,^{1,2} and that of 22 cm^{-1} in the non-(metal-metal bonded) compound $\text{Mn}_2(\text{CO})_8(\text{PMe}_2)_2$ ^{4,5}]. The data therefore support structure (a) in the Figure, in which Mn^{I} and Re^{I} are in their normal octahedral low-spin environments.

The 18-electron rule can then be satisfied in one of two ways. The sulphur atom of the RS^- group could be using all three lone-pairs to fill the a_1 and e orbitals of one face of the M_4 tetrahedron. In this case the ligand is formally a five-electron donor, and S is presumably tetrahedral, with the S-R bond normal to the M_3 plane to which it is bound. Less probably, the ligand could be a 1-electron donor, filling only the a_1 set, with

the S-R bond almost parallel to the face; this would give a positive M-M bond-order, and some deviation from tetrahedral symmetry, both of which seem less consistent in detail with the experimental data.

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