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# The Vibrational Spectra and Structures of the Organothiotricarbonylrheniums and Related Species

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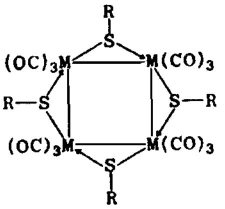
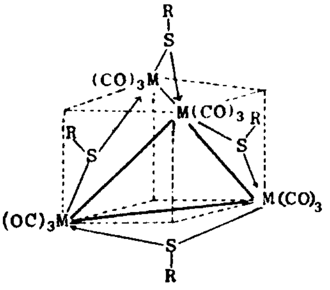
*Infrared and Raman spectra of* $[Re(CO)_3X]_4$ *(*$X = SCH_3$, $SC_6H_5$ *and* $SeC_6H_5$*) are reported. These* have been assigned on the basis of $T_d$ symmetry by *analogy with our measurements on* $Ir_4(CO)_{12}$. *This suggests that the compounds* $[Re(CO)_3X]_4$ *have a tetrahedron of metal atoms with X over the centre of the triangular faces. The absence of intense bands in the required region of the Raman spectrum of* $[Re(CO)_3SCH_3]_4$ *lends support for the idea of little or no metal-metal interaction in such a structure.*

## Introduction

When initially prepared,[1,2] the organothiotricarbonyls of manganese and rhenium were characterised as trimers by solution molecular weight studies. Subsequent solution studies[3,4] and mass spectroscopic[3,4] data suggested a tetrameric formulation, and despite the enigmatic solution data[3] for these complexes, the weigth of evidence for the organothiotricarbonylmanganese complexes now favours tetramers. Our own mass spectra of the organothio-[5] and organoseleno-[6] tricarbonyls of rhenium indicate a tetrameric formulation.



I



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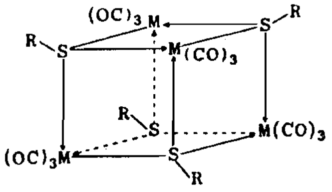

III

Three possible structures have been discussed[3,4,6,7,8] for these tetramers, and mass spectroscopic evidence claims[4] to favour (II). On the basis of the carbonyl region infrared spectra, however, (I) or (III) appear the more likely, and the metal carbonyl binary combination infrared spectra have been adequately interpreted[7] using structure (III). We now report full range infrared and Raman data for $[CH_3SRe(CO)_3]_4$, $[C_6H_5SRe(CO)_3]_4$ and $[C_6H_5SeRe(CO)_3]_4$ as further evidence of structure (II) for this class of complexes.

## Experimental Section

*Raman Spectra.* These were recorded on a Cary 81 Laser Raman Spectrometer. Solids were run as fine powders in glass sample tubes, and no spurious peaks from the glass were found. Only $[C_6H_5SRe(CO)_3]_4$ was sufficiently soluble to give a solution spectrum, and this was obtained in carbon tetrachloride in a 0.5 mm. diameter tube viewed « end-on ». Errors in quoted Raman frequencies are estimated at $\pm 2$ cm$^{-1}$.

*Infrared Spectra.* These were obtained in the 5000-200 cm$^{-1}$ region on a Perkin-Elmer model 225 Spectrophotometer calibrated with the spectrum of water vapour. Below 200 cm$^{-1}$ frequencies were obtained from the Grubb-Parsons Interferometer by Mr. Roger Barr. Frequencies are believed to be $\pm 1$ cm$^{-1}$.

## Results and Discussion

The observed frequencies of $[CH_3SRe(CO)_3]_4$, $[C_6H_5SRe(CO)_3]_4$, $[C_6H_5SeRe(CO)_3]_4$ and $Ir_4(CO)_{12}$ in the metal carbonyl stretching region are listed in Table I, and those of $[CH_3SRe(CO)_3]_4$ and $Ir_4(CO)_{12}$ below 700 cm$^{-1}$ are in Table III. Due to our inability to obtain solution Raman spectra of all complexes but $[C_6H_5SRe(CO)_3]_4$, a full comparison of

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

(2) A. G. Osborne and F. G. A. Stone, *Chem. Comms.*, (1965) 361, and *J. Chem. Soc.*, (1966) 1143.

(3) B. F. G. Johnson, P. J. Pollick, I. G. Williams and A. Wojcicki, *Inorg. Chem.*, 7, 831 (1968).

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

(5) E. W. Abel and M. I. Bruce, unpublished observations.

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**Table I.** The Infrared and Raman Spectra of $[CH_3SRe(CO)_3]_4$, $[C_6H_5SRe(CO)_3]_4$, $[C_6H_5SeRe(CO)_3]_4$ and $Ir_4(CO)_{12}$ in the Metal Carbonyl Stretching Region

| | Solution Infrared ($CCl_4$) | Fundamentals $^a$ from Combinations | Solid $^b$ State Infrared | Solid $^b$ State Raman | Assignment |
|---|---|---|---|---|---|
| $[CH_3SRe(CO)_3]_4$ | | | | | |
| | | 2052 | | 2059 (35) | $A_1$ |
| | 2028 | 2028 | 2026 (100) | | $T_2{}^1$ |
| | | 1955 | 1960 (sh) | 1959 (100) | E |
| | 1944 | 1945 | 1943 (60) | 1944 (30) | $T_2{}^2$ |
| | | 1924 | 1924 (80) | 1921 (10) | $T_1$ |
| $[C_6H_5SeRe(CO)_3]_4$ | | | | | |
| | | 2054 | | 2059 (35) $^d$ | $A_1$ |
| | 2032 | 2030 | 2026 (100) | 2030 (4) | $T_2{}^1$ |
| | | 1959 | 1965 (sh) | 1968 (100) $^d$ | E |
| | 1945 | 1944 | 1945 (90) | 1944 (90) $^d$ | $T^2$ |
| | | 1929 | 1923 (50) | 1925 (25) | $T_1$ |
| $[C_6H_5SeRe(CO)_3]_4$ | | $^c$ | | 2054 (55) | $A_1$ |
| | 2030 | | 2028 (100) | | $T_2$ |
| | | | 1964 (sh) | 1954 (100) | E |
| | 1945 | | 1942 (90) | 1940 (85) | $T_2{}^2$ |
| | | | 1921 (55) | 1922 (10) | $T_1$ |
| $Ir_4(CO)_{12}$ | | $^c$ | 2110 (1) | 2111 (50) | $A_1$ |
| | | | 2075 (sh) | | $C^{13}O$ |
| | 2071 | | 2066 (100) | 2070 (4) | $T_2{}^1$ |
| | 2032 | | 2030 (80) | 2030 (30) | $T_2{}^2$ |
| | | | 2010 (sh) | 2010 (100) | E |
| | | | 2005 (30) | 2004 (10) | $T_1$ |

$^a$ See Table 2 for combination spectra. $^b$ Numbers in brackets refer to approximate relative intensities with the strongest band in this region valued at 10. $^c$ Due to low solubility reliable values were not obtainable. $^d$ Bands are observed at 2055, 1960 and 1944 $cm^{-1}$ in the solution Raman spectrum.

**Table II.** The Infrared Spectra of $[CH_3SRe(CO)_3]_4$ and $[C_6H_5SRe(CO)_3]_4$ in the Metal Carbonyl Binary Combination Region.

| | Band | Relative Intensity | |
|---|---|---|---|
| $[CH_3SRe(CO)_3]_4$ | | | |
| | 4080 | 90 | $A_1+T_2{}^1$ |
| | 4056 | 80 | $2T_2{}^1$ |
| | 3997 | 40 | $A_1+T_2{}^2$ |
| | 3971 | 80 | $T_2{}^1+T_2{}^2$ |
| | 3949 | 100 | $T_1+T_2{}^1$ |
| | 3906 | 5 | $E+T_2{}^2$ |
| | 3890 | 60 | $2T_2{}^2$ |
| | 3870 | 10 | $T_1+T_2{}^2$ |
| | 3848 | 65 | $2T_1$ |
| $[C_6H_5SRe(CO)_3]_4$ $^a$ | | | |
| | 4084 | 100 | $A_1+T_2{}^1$ |
| | 4060 | 85 | $2T_2{}^1$ |
| | 4000 | 50 | $A_1+T_2{}^2$ |
| | 3974 | 80 | $T_2{}^1+T_2{}^2$ |
| | 3956 | 100 | $T_1+T_2{}^1$ |
| | 3903 | 10 | $E+T_2{}^2$ |
| | 3889 | 50 | $2T_2{}^2$ |
| | 3874 | 20 | $T_1+T_2{}^2$ |
| | 3858 | 60 | $2T_1$ |

$^a$ The spectrum of benzenethiol showed only very weak bands in this region, which were readily subtractable from the spectrum of $[C_6H_5SRe(CO)_3]_4$.

**Table III.** Low Energy Infrared and Raman Spectra of $Ir_4(CO)_{12}$ and $[CH_3SRe(CO)_3]_4$.

| $Ir_4(CO)_{12}$ | | $[CH_3SRe(CO)_3]$ | |
|---|---|---|---|
| Raman | Infrared | | |
| 542 (3) | 544 (sh) | 680 (1) | 625 (95) |
| 530 (1) | 529 (95) | 670 (1) | 614 (90) |
| 513 (0·5) | 494 (100) | 635 (4) | 610 (85) |
| 470 (1·5) | 480 (50) | 624 (6) | 588 (15) |
| 459 (30) | 467 (80) | 584 (1) | 518 (100) |
| 450 | | 501 (100) | 513 (75) |
| 437 (4) | 439 (90) | 485 (5) | 484 (75) |
| 430 (sh) | 428 (60) | 470 (2) | 476 (7) |
| 365 (1·5) | | 338 (6) | 469 (75) |
| 208 (70) | | 321 (60) | 389 (6) |
| 164 (85) | 162 | 280 (4) | |
| 133 (10) | | 232 (10) | 229 (60) |
| 105 (100) | | 156 (20) | |
| 93 (80) | | 123 (50) | |
| 82 (15) | | 88 (66) | |
| 65 (15) | | | |

the solution infrared ,the solid state infrared and the solid state Raman spectra was necessary. Thus, although it is usually difficult to make assignments from solid state spectra without knowledge of site symmetry, here we believe that we have sufficient evidence to complete a full assignment of the metal carbonyl stretching region, and also some of the bands of lower frequency.

The observed overtones and combinations of $[CH_3SRe(CO)_3]_4$ and $[C_6H_5SRe(CO)_3]_4$ utilised to derive the fundamentals of column 3 Table I are in Table II.

*Carbonyl Stretching Region.* Table IV outlines the number and type of metal carbonyl stretching modes predicted for the tree structures I, II and III of the organothio- and organoseleno-tricarbonylrheniums, together with the number of infrared active binary combinations.

**Table IV.** Predicted Numbers of Metal Carbonyl Stretching Modes Associated with. Each of the Three Structures I, and III Illustrated.

| Structure | Point Group | Active Raman Modes | Active Infrared Modes | Inactive Modes | Number of Infrared Active Binary Combinations |
|---|---|---|---|---|---|
| I | $D_{4h}$ | 5<br>$(2A_{1g}+2B_{1g}+Eg)$ | 3<br>$(A_{2u}+2Eu)$ | 1<br>$(B_{2u})$ | 14 |
| II | $D_{2d}$ | 8<br>$(2A_1+B_1+2B_2+3E)$ | 5<br>$(2B_2+3E)$ | 1<br>$(A_2)$ | 17 |
| III | $T_d$ | 4<br>$(A_1+E+2T_2)$ | 2<br>$(2T_2)$ | 1<br>$(T_1)$ | 10 |

Refering to Table I we note that the observed bands in all of the complexes are three strong and two weak absorptions in the solid state Raman, two strong absorptions in the solution infrared and three absorptions (all co-incident with Raman bands) in the solid state infrared spectra. Coupled with the further evidence presented below, the observed spectra strongly support structure (III), and the deviations from the predictions of $T_d$ symmetry in the solid state spectra also occur in $Ir_4(CO)_{12}$ which is of known[9] $T_d$ symmetry.

The totally symmetric (A), mode is uniquely assigned[10] at higher energy than all others, and both $T_2^1$ modes are readily assigned to the two bands appearing in the solution infrared spectra. The appearance of a third strong band in the solid state infrared spectrum could be due to further splitting of the $T_2{}^2$ mode (derived from the E mode of the $M(CO)_3$ unit), or more likely (as no other new strong or medium bands arise in the solid state infrared spectrum), is due to the activation of the ideally inactive $T_1$ mode. This mode alone, of those inactive in strictly $T_d$ symmetry would be expected to become active on a slight distortion from $T_d$ towards an overall $D_{2d}$ symmetry in the solid.

The very low intensity (and even non-appearance in two cases) of the $T_2{}^1$ mode in the Raman spectra is inexplicable to us, and is comparable to the similar behaviour[11] of the E mode in the $M(CO)_5X$ (M = Mn and Re) types. The strongest band in the metal carbonyl stretching region in the Raman spectra of these $[Re(CO)_3X]_4$ complexes is the E mode, a parallel situation to that in the octahedral metal hexacarbonyls[12] where the $E_g$ mode is more intense than the $A_{1g}$. If these assignments of the solid state spectra are correct (and we presently find no cause for doubt), the small shifts observed in the frequencies for solid state and solution spectra are remarkable.

Although the relative intensities of the carbonyl stretching modes are similar for what we believe to be the closely related $[Re(CO)_3SR]_4$ types and $Ir_4(CO)_{12}$, there are noteworthy differences in band positions. As previously noted,[7] the separation of the $A_1$ mode from the next highest mode for these rhenium complexes ($\sim$30 cm$^{-1}$) is smaller than in such species known to have metal-metal bonds. (*e.g.* $\sim$40 cm$^{-1}$ in $Ir_4(CO)_{12}$). Further, in $Ir_4(CO)_{12}$ we find the $T_2$ modes adjacent to one another, but are separated by the E mode in $[RSRe(CO)_3]_4$ and $[RSeRe(CO)_3]_4$. This supports the proposal[7] of low interaction constants between carbonyl groups on different metal atoms in the $[RSRe(CO)_3]_4$ and $[RSeRe(CO)_3]_4$ molecules, compared to such interactions in compounds with strong metal-metal bonds. This further supports structure III which has no formal metal-metal bonds.

*Low Energy Infrared and Raman Spectra.* In the region 700-350 cm$^{-1}$ the tetrahedral $M_4(CO)_{12}$ species would be expected to have 10 and 5 active bands in the Raman and infrared spectra respectively, derived from six δ(MCO) bending vibrations $(A_1+2E+3T_2)$ and four ν(CO) stretching vibrations $(A_1+E+2T_2)$. Whilst assignment in this region is difficult, it is not unreasonable to assign in $Ir_4(CO)_{12}$ the five very strong infrared bands in this region to the $T_2$ modes, though these cannot be separated specifically into ν(MC) and δ(MCO) modes. Four of these co-incide with bands in the Raman spectrum, but despite the observation of nine of the expected ten Raman bands, only one other band in addition to these $T_2$ modes can be assigned with any confidence. This is the most intense of these Raman bands at 459 cm$^{-1}$ and by analogy with other Raman spectra of metal carbonyls is assigned as the $A_1$ (M-C) stretch.

Assignments for $[CH_3SRe(CO)_3]_4$ in this region are complicated by the possible presence of ν(S-CH$_3$) modes, thus a very strong band at 731 cm$^{-1}$ in the Raman spectrum is believed to be the $A_1$, ν(S-CH$_3$) mode, and from a comparison with the infrared spectrum of $[CH_3SMn(CO)_3]_4$ the band at $\sim$625 cm$^{-1}$ in the infrared and Raman spectrum of $[CH_3SRe(CO)_3]_4$ could be assigned as essentially due to the $T_2$, ν(S-CH$_3$) mode. The remaining five strong bands at 614, 588, 518, 484, and 469 cm$^{-1}$ in the infrared spectrum are tentatively assigned as the $T_2$, ν(M-C) and δ(MCO) vibrations. There is a shortage of bands in this region of the Raman spectrum, and the only assignments which to us appear reasonable are $A_1$ ν(M-C) at 501 cm$^{-1}$ and various $T_2$ δ(MCO) or ν(M-C) absorptions at 584, 485 and 470 cm$^{-1}$ .

The assignment[13] of the very strong bands at 208, 164 and 105 cm$^{-1}$ in the Raman spectrum of $Ir_4(CO)_{12}$ has already been made to the $A_1$, $T_2$ and E modes respectively. Confirmation of this is now to hand

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(7) P. S. Braterman, *Chem. Comm.*, (1968), 91 and *J. Chem. Soc.* (A) 1968 in press.

(8) E. W. Abel and B. C. Crosse, *Organometallic Chemistry Reviews*, *2*, 451 (1967).

(9) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, *88*, 1821 (1966).

(10) P. S. Braterman and D. T. Thompson, *J. Organometal. Chem.*, *10*, P11 (1967).

(11) See e. g. I. J. Hyams, D. Jones and E. R. Lippincott, *J. Chem. Soc.* (A), 1987 (1968).

(12) E. W. Abel, R. A. N. McLean, S. P. Tyfield, P. S. Braterman, A. P. Walker and P. J. Hendra, *J. Mol. Spec.*, in press, and references therein.

from our far infrared spectrum in which only one strong band at 162 $cm^{-1}$ is present below 200 $cm^{-1}$. Other weak bands which we observe between 200 and 50 $cm^{-1}$ can be assigned to δ(C-M-C) or lattice modes.

It must be emphasised that in $Ir_4(CO)_{12}$, as in other metal-metal bonded clusters, the bands assigned to metal-metal stretching vibrations in the Raman spectra are more intense than any of the higher energy bands and of notably higher intensity than the $A_1$ ν(M-C) mode. In the light of this, the absence of any band stronger than that for $A_1$ ν(M-C) in the 200-50 $cm^{-1}$ region in the spectra of $[CH_3SRe(CO)_3]_4$, $[C_6H_5SRe(CO)_3]_4$ and $[C_6H_5SeRe(CO)_3]_4$ presents further strong evidence for the absence of strong metal-metal interaction in these complexes, and reinforces support for structure III.

The intensities of the three lowest bands are fairly appreciable, and the frequencies are not far from the ratios 2: $\sqrt{2}$: 1 predicted for a tetrahedral metal-metal bonded cluster.[13] Although this could possibly indicate some metal-metal interaction, a number of simple $M(SCH_3)_n$ compounds are known to have two or three fairly strong bands below 160 $cm^{-1}$.[14] It is likely that vibrations of a similar nature are causing the absorptions in $[Re(CO)_3SCH_3]_4$.

The four Raman bands between 350 and 200 $cm^{-1}$ in $[CH_3SRe(CO)_3]_4$ are also believed to all involve the $CH_3S$ group.

## Conclusion

Overall, our results support the deductions[7] from the infrared combination spectra that these tetrameric organothio- and selenotricarbonyls of rhenium have structure III. In this structure there appears to be no formal metal-metal interaction, and the organothio- and organoseleno groups behave as terdentate bridging groups.

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