double bond in the ligand aids the nitrile group in back-accepting charge from the metal, resulting in a smaller increase in the CN stretching frequency. For $(CH_2CHCN)_2Mo(CO)_2$, one may note at least two effects which operate to *lower* the bond order of the CN group and thus offset any shift to high frequency which might have been brought about through coordination. In the first place, if the olefinic group of the acrylonitrile molecule is coordinated to a metal, this may improve its ability to enhance back acceptance by the coordinated nitrile group. Also, in bis(acrylonitrile)-molybdenum dicarbonyl there may be a greater amount of charge on the metal to back donate to the ligands owing to a reduced number of carbonyls compared to $(CH_2CHCN)W(CO)_5$.[10] For further illustration, one may consider bis(acrylonitrile)nickel, in which there are no carbonyls to serve as π-acceptors so the ligand must back accept all the charge from the metal, and the C≡N frequency reflects this by showing the greater shift to lower frequency (−35 cm.$^{-1}$).[2] The CN position in $(CH_2CHCN)_2Mo(CO)_2$ thus appears only slightly shifted to lower frequency, 2220 cm.$^{-1}$, compared to its position in the free ligand, 2235 cm.$^{-1}$, even though it is coordinated to the metal atom.

Conclusions

It is concluded that the structure of bis(acrolein)-molybdenum dicarbonyl is polymeric with the ligands bridging adjacent metal atoms by π-complexing through the C═C and C═O groups. A metastable soluble form, first obtained, readily polymerizes to an insoluble bridged structure. Spectral data suggest a near-planar configuration of the ligands.

The proposed structure is in keeping with the solubility properties, a reasonable coordination number of the metal, and reactivity of the compounds. The diamagnetism and infrared and nuclear magnetic resonance spectral evidence strongly support these conclusions and also permit explanation of the structures of previously reported bis(acrylonitrile)molybdenum dicarbonyl,[7] bis(acrylonitrile)nickel,[2] and bis-(acrolein)nickel.[2] In the acrylonitrile complexes it is proposed that the nitrile group involvement is through the nitrogen lone-pair electrons.

The relative shifts in the infrared stretching frequencies of the coordinated C═C, C═O, and C≡N groups may be explained qualitatively by consideration of the ability of the ligand to accept back-donation from the metal dπ orbitals in the various complexes.

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Vibrational Spectra and Bonding in Metal Carbonyls. IV. CO and Re–Re Stretching Modes in the Decacarbonyls of Rhenium and Manganese[1]

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The Raman spectrum of $Re_2(CO)_{10}$ has been recorded as well as the infrared spectra of both dimanganese and dirhenium decacarbonyls in the region of CO stretching overtones. With these data and the existing infrared data, the problem of interaction of CO stretching motions across the metal–metal bond has been examined. It has been found that the spectrum of CO stretching frequencies may be satisfactorily explained using a potential energy function based upon a simple physical model in which a repulsive interaction between the dπ electrons of the two metal atoms is invoked. The Re–Re stretching frequency is 120 cm.$^{-1}$, corresponding to a force constant of about 0.8 mdyne/Å.

Introduction

The question of the nature and magnitude of the interaction between the two $M(CO)_5$ halves of an $(OC)_5MM(CO)_5$ molecule or between the two $M(CO)_4L$ halves of an $L(OC)_4MM(CO)_4L$ molecule is an important and interesting one which has concerned us for some time. From a comparison of the infrared spectra[2,3] of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ with those of corresponding $XM(CO)_5$ compounds[4] it is apparent that there are several characteristic differences, which are not so simple as a mere shifting of the pattern as a whole. These differences are, chiefly: (1) The highest frequency band is relatively very weak in $XM(CO)_5$ compounds, whereas it has an intensity intermediate between those of the other two bands in the dinuclear species. (2) The relative spacings of the three bands differ in the mononuclear and binuclear

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(1) Supported by the National Science Foundation.

(2) F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 141 (1956).

(3) N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **3**, 1123 (1964).

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TABLE I

INFORMATION PERTAINING TO CO STRETCHING MODES OF AN $XM(CO)_5$ OR $M(CO)_5$ GROUP WITH C_{4v} SYMMETRY

Symmetry species[a]	Symmetry coordinates[b]	Secular equations
A_1 (R, IR)	$S_1 = {}^1/_2(\Delta_2 + \Delta_3 + \Delta_4 + \Delta_5)$ $S_2 = \Delta_1$	$\begin{vmatrix} \mu(k_2 + 4ki) - \lambda & 2\mu k_i \\ 2\mu k_i & \mu k_i - \lambda \end{vmatrix} = 0$
B_1 (R)	$S_3 = {}^1/_2(\Delta_2 - \Delta_3 + \Delta_4 - \Delta_5)$	$\lambda = \mu k_2$
E (R, IR)	$S_{4a} = 1/\sqrt{2}(\Delta_2 - \Delta_4)$ $S_{4b} = 1/\sqrt{2}(\Delta_3 - \Delta_5)$	$\lambda = \mu(k_2 - 2k_i)$

[a] Activities in parentheses; R = Raman, IR = infrared. [b] See Figure 1 for numbering system; Δ_i refers to increment in the ith CO distance.

compounds, mainly in the position of the highest frequency band relative to the other two. In $XM(CO)_5$ compounds it lies some 80–120 cm.$^{-1}$ above the middle band, while in the dinuclear carbonyls it lies only 30–60 cm.$^{-1}$ above the middle band.

In this paper we present a treatment of the relationship between the spectra of $XM(CO)_5$ molecules and $(OC)_5MM(CO)_5$ molecules which is based on the simple physical idea that there should be a repulsive interaction between the dπ electrons in the two $M(CO)_5$ halves of the dinuclear carbonyls. We shall show that a potential energy function for the CO stretching modes of the molecule derived in a very simple way from this assumption leads to secular equations which account very satisfactorily for the entire set of observed CO stretching frequencies and which also explain the two characteristic features mentioned above. The necessary experimental data have been derived from the Raman spectra of $Re_2(CO)_{10}$, which is white, and from the infrared active combinations and overtones of $Mn_2(CO)_{10}$, for which Raman measurements were impossible because of its color. The combinations and overtones have also been measured for $Re_2(CO)_{10}$ and shown to be entirely consistent with the assignment of the directly observed fundamentals. Finally, from the Raman spectrum of $Re_2(CO)_{10}$, the frequency of the Re–Re stretching mode has been ascertained. A more complete discussion of the vibrational spectrum of $Re_2(CO)_{10}$, supported by a normal coordinate analysis of the entire spectrum, will be reported elsewhere. The applicability of the ideas developed here to various $L(OC)_4MM(CO)_4L$ compounds[5] and to $I(OC)_4FeFe(CO)_4I$[6] will also be reported in another paper.

Derivation of Equations

In order to treat the binuclear carbonyls as two interacting $M(CO)_5$ groups, it is obviously necessary to have at the beginning a good understanding of the CO frequencies of the $M(CO)_5$ moiety itself. Fortunately, as a result of previous experimental[4,7] and theoretical[8,9] studies of $XM(CO)_5$ compounds, we have such an understanding, which may be adequately summarized, for the present purpose, as follows. An $XM(CO)_5$ or $M(CO)_5$ molecule with C_{4v} symmetry should have the CO stretching modes indicated in Table I. From the previous studies of $XM(CO)_5$ molecules[7-9] we know that the highest frequency infrared band corresponds essentially to the symmetry coordinate S_1, that the intense band of intermediate frequency corresponds to the degenerate mode with the symmetry coordinates S_{4a}, S_{4b}, and that the lowest energy band corresponds to the mode with the symmetry coordinate S_2. It has been shown that such an assignment leads to force constants[9c] which are physically reasonable and also that the relative intensities agree qualitatively with this assignment.[8] Moreover, using force constants obtained solely from the observed infrared bands the frequency of the B_1 mode can be calculated and hence the entire Raman spectrum predicted. In several cases the Raman spectra have now been recorded,[7] and they agree very well with the predictions.

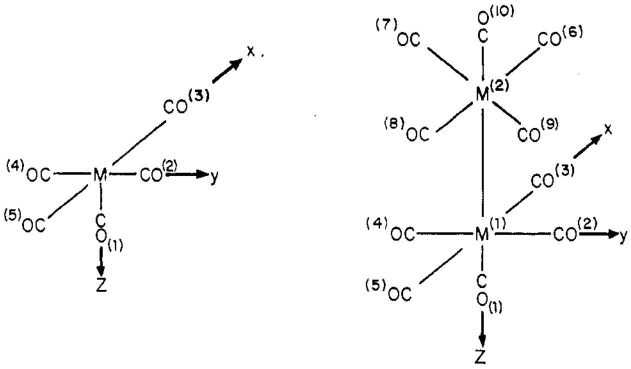

Figure 1.—The numbering system used for the $M(CO)_5$ and $M_2(CO)_{10}$ groups.

For an $(OC)_5MM(CO)_5$ molecule, with the structure that the rhenium and manganese carbonyls are known to have,[10] a numbering scheme is given in Figure 1. Table II summarizes our analysis of the CO stretching vibrations. The symmetry species were derived and the expressions for the symmetry coordinates were constructed by standard methods. The secular equations were obtained using a model which embodies the principal idea of this paper and which will now be explained.

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TABLE II

INFORMATION PERTAINING TO CO STRETCHING MODES OF AN $M_2(CO)_{10}$ MOLECULE WITH D_{4d} SYMMETRY

Symmetry species[a]	Symmetry coordinates[b]	Secular equations
A_1 (R)	$R_1 = 1/\sqrt{8}(\Delta_2 + \Delta_3 + \Delta_4 + \Delta_5 + \Delta_6 + \Delta_7 + \Delta_8 + \Delta_9)$	$\begin{vmatrix} \mu(k_2 + 4k_i + 2K) - \lambda & 2\mu k_i \\ 2\mu k_1 & \mu(k_i + k_j) - \lambda \end{vmatrix} = 0$
	$R_2 = 1/\sqrt{2}(\Delta_1 + \Delta_{10})$	
B_2 (IR)	$R_3 = 1/\sqrt{8}(\Delta_2 + \Delta_3 + \Delta_4 + \Delta_5 - \Delta_6 - \Delta_7 - \Delta_8 - \Delta_9)$	$\begin{vmatrix} \mu(k_2 + 4k_i - 2k) - \lambda & 2\mu k_i \\ 2\mu k_i & \mu(k_i - k_j) - \lambda \end{vmatrix} = 0$
	$R_4 = 1/\sqrt{2}(\Delta_1 - \Delta_{10})$	
E_1 (IR)	$R_{5a} = 1/\sqrt{8}(\sqrt{2}\Delta_2 - \sqrt{2}\Delta_4 + \Delta_6 - \Delta_7 - \Delta_8 + \Delta_9)$	$\lambda = \mu(k_2 - 2k_i + \sqrt{2}K)$
	$R_{5b} = 1/\sqrt{8}(\sqrt{2}\Delta_3 - \sqrt{2}\Delta_5 + \Delta_6 + \Delta_7 - \Delta_8 - \Delta_9)$	
E_2 (R)	$R_{6a} = 1/2(\Delta_2 - \Delta_3 + \Delta_4 - \Delta_5)$	$\lambda = \mu k_2$
	$R_{6b} = 1/2(\Delta_6 - \Delta_7 + \Delta_8 - \Delta_9)$	
E_3 (R)	$R_{7a} = 1/\sqrt{8}(\sqrt{2}\Delta_2 - \sqrt{2}\Delta_4 - \Delta_6 + \Delta_7 + \Delta_8 - \Delta_9)$	$\lambda = \mu(k_2 - 2k_i - \sqrt{2}K)$
	$R_{7b} = 1/\sqrt{8}(\sqrt{2}\Delta_3 - \sqrt{2}\Delta_5 - \Delta_6 - \Delta_7 + \Delta_8 + \Delta_9)$	

[a] Activities in parentheses: R = Raman; IR = infrared. [b] See Figure 1 for numbering system; Δ_i refers to increment in the ith CO distance.

Insofar as interactions between CO stretches within each $M(CO)_5$ group are concerned, we use exactly the same model as previously described for mononuclear carbonyls in general.[9] The coupling between CO stretching motions in different $M(CO)_5$ groups has been introduced using two additional interaction force constants, K and k_j. The constant K pertains to the interaction between the stretching of one of the eight equivalent oscillators, *i.e.*, Δ_i (i = 2–9), and the stretching of one of the other two members of this set on the other metal atom which are nearest to it. For example, the potential energy expression contains the terms $K\Delta_2\Delta_9$ and $K\Delta_2\Delta_6$ but *not* the terms $K\Delta_2\Delta_7$ and $K\Delta_2\Delta_8$. The interaction constant k_j is the coefficient of the terms $\Delta_1\Delta_{10}$ and $\Delta_{10}\Delta_1$ in the potential energy expression.

It can be seen in Table II that the symmetry coordinates R_1 and R_3 are just the symmetric and antisymmetric combinations of the symmetry coordinates of the type S_1 for each half of the molecule, while R_2 and R_4 are the symmetric and antisymmetric combinations of the symmetry coordinates of the type S_2 for $M(CO)_5$. Consequently, the secular equations for the A_1 (ν_1, ν_2) and B_2 (ν_3, ν_4) modes of $M_2(CO)_{10}$ each reduce to the secular equation of the A_1 modes (ν_1, ν_2) of $M(CO)_5$ when the interaction constants K and k_j are set equal to zero. Similarly, the E_1 and E_3 modes of $M_2(CO)_{10}$ are symmetric and antisymmetric combinations, respectively, of the E modes of the two $M(CO)_5$ groups and their secular equations differ from those for the latter modes only in the presence of the interaction constant K. The E_2 mode of $M_2(CO)_{10}$ is a combination of the B_1 modes of the two $M(CO)_5$ groups, but because of the nature of the E_2 mode, as expressed in the symmetry coordinates R_{6a},R_{6b}, no interaction constant occurs in the secular equation which is therefore identical with that for the B_1 mode of an $M(CO)_5$ group.

It will now be shown that for physical reasons both of the end-to-end interaction constants, K and k_j, should be positive, using arguments similar in principle to those used previously[9a] with respect to the sign of the interaction constant k_i. We shall refer to Figure 2, in which a portion of the $M_2(CO)_{10}$ molecule is shown. In this sketch, however, the molecule is distorted, by means of an internal rotation of 45°. Thus, $CO^{(2)}$ and $CO^{(6)}$ are shown as coplanar. It will be demonstrated at the end that the argument given for this configuration applies equally well to the actual situation.

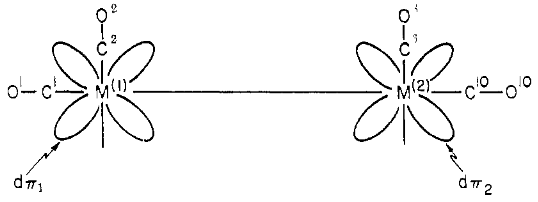

Figure 2.—A sketch to show the interaction between dπ electrons of the two metal atoms.

On each metal atom there are filled dπ orbitals which can be designated d_{xz} and d_{yz} if the molecular axis is called the z axis. To a certain extent, the electron density in these orbitals is delocalized into the appropriate pπ orbitals of the C and O atoms of the carbonyl groups, thus forming M–C π bonds, but still, there is a repulsive interaction between electron density in dπ orbitals of one metal atom with that in dπ orbitals of the other. To the extent that vibrational motions alter the magnitude of the electron density in these dπ orbitals, the repulsive force will be altered, and, conversely, the presence of this repulsive force can affect different vibrational modes in different ways and to different degrees. Let us suppose that the bond C^2–O^2 is stretched. Then, as explained earlier,[9a] the M^1–C^2 bond becomes stronger, meaning that electron density in $d\pi_1$ enters to a greater extent into a bonding π orbital for M^1–C^2. Because of the repulsive interaction between electrons in $d\pi_1$ and those in $d\pi_2$, the removal of electron density from $d\pi_1$ tends to stabilize the electrons in $d\pi_2$, thus lessening their tendency to enter into π bonding between M^2 and C^6. But, as the M^2–C^6 π bonding is weakened, the C^6–O^6 π bonding is strengthened. It is therefore more difficult to stretch C^2–O^2 and C^6–O^6 simultaneously than to stretch either one separately, which means that the coefficient of the term $\Delta_2\Delta_6$ (and all comparable terms) in the potential energy function must be positive. The coefficient in question is, of course, K. The same type of argument can be used to show that k_j is positive.

The argument given in the preceding paragraph for the coplanar $CO^{(2)}$ and $CO^{(6)}$ groups will hold equally

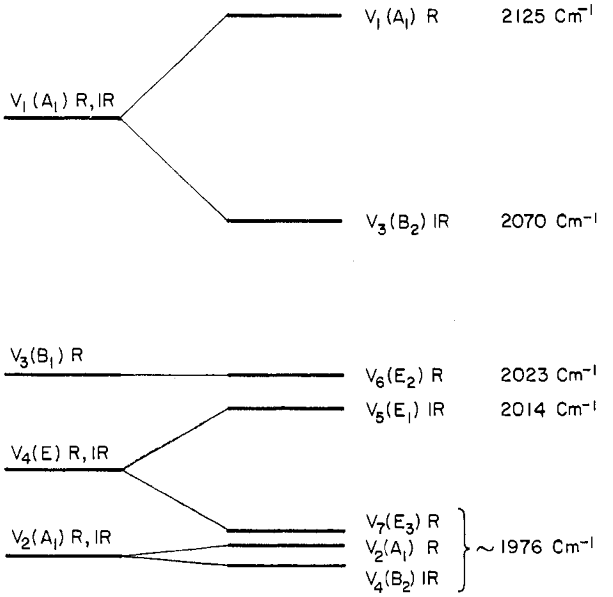

Figure 3.—A diagram showing how the CO stretching spectrum of $M_2(CO)_{10}$ (right) is derived from that of the $M(CO)_5$ groups (left) composing it. The numerical values of the frequencies at the far right are for $Re_2(CO)_{10}$.

well (though it is less conveniently represented in a sketch) for the actual staggered arrangement. This is so because any given pair of degenerate dπ orbitals, such as those we have been discussing, are mathematically and *physically* equivalent to any normalized linear combination of themselves, and, in particular, to the linear combinations $2^{-1/2}(d_{xz} + d_{yz})$ and $2^{-1/2}(d_{xz} - d_{yz})$, which correspond to two dπ orbitals rotated by 45° to the original ones.

Using the secular equations in Tables I and II and setting the constants K and k_j positive, we can construct a diagram showing qualitatively how the frequencies of the CO stretching modes of $M_2(CO)_{10}$ will be related to the modes of the $M(CL)_5$ moieties from which they are considered to be derived. Figure 3 shows such a diagram. Actually, without experimental data, the relative differences in frequencies could not in general be estimated; the intervals in Figure 3 are based on the assignments of experimental frequencies to be discussed presently. It can be seen, however, that the *qualitative* discussion given up to this point enables us to account for the two major differences between $XM(CO)_5$ and $M_2(CO)_{10}$ infrared spectra pointed out in the Introduction.

The highest frequency infrared band in $XM(CO)_5$ owes its intensity to a component of change in dipole moment in the Z direction (see Figure 1). Only to the extent that the four equivalent CO groups are bent out of the xy plane and/or to the extent that the actual normal mode responsible for this high-frequency band contains an admixture of the symmetry coordinate S_1 with S_2 (or some other A_1 mode of the molecule) will the band have infrared intensity. Both of these effects are rather small and the band is therefore weak. In the binuclear species, however, the corresponding infrared mode, which also depends for its intensity

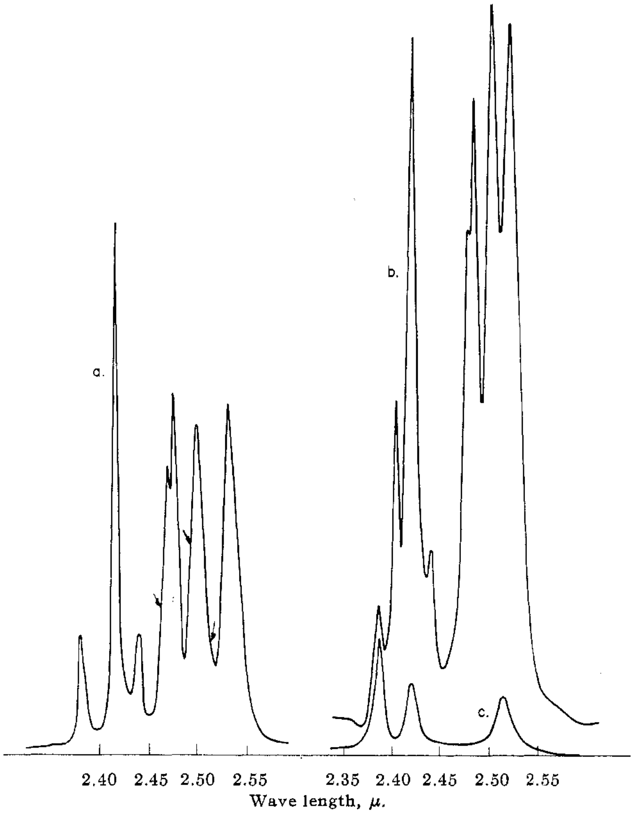

Figure 4.—Near-infrared spectra in CCl_4: a, $Re_2(CO)_{10}$; b, $Mn_2(CO)_{10}$ with $ClMn(CO)_5$ contamination; c, $ClMn(CO)_5$. Note: Under higher resolution, shoulders appear at positions marked with small arrows (see Table VB).

on a component of change in dipole moment in the Z direction, can get intensity not only in the two ways mentioned for the mononuclear species but also by another, and presumably more powerful, mechanism. According to the argument used above to show that K is positive, when the four equivalent CO groups on metal atom M_1 stretch in phase while the four on the other metal atom, M_2, contract in phase, electron density flows out of dπ_1 and into dπ_2. Thus a dipole moment is induced in the z direction, and the infrared intensity of this vibration, ν_3, is enhanced. The fact that the high-frequency infrared band is much lower in energy relative to the other two bands for $M_2(CO)_{10}$ molecules than for the $XM(CO)_5$ molecules is seen from Figure 4 to be a direct consequence of the coupling which produces ν_1 and ν_3, given that the sign of the interaction constant K is positive. The fact that the separation increases from 31 cm.$^{-1}$ in $Mn_2(CO)_{10}$ to 48 cm.$^{-1}$ in $Tc_2(CO)_{10}$ to 56 cm.$^{-1}$ in $Re_2(CO)_{10}$ is also easily and naturally explained, since the increasing length of the metal–metal bond[10] in the same direction leads to a decreasing repulsive interaction between electrons in the filled dπ orbitals.

Complete Assignment of CO Stretching Modes

Table III lists the observed infrared and Raman CO stretching modes of $Re_2(CO)_{10}$. The Raman spectrum is shown in Figure 5. Also listed in Table III are our assignments which we shall now explain. From the

TABLE III

OBSERVED[a] AND CALCULATED[b] CO STRETCHING MODES OF $M_2(CO)_{10}$ MOLECULES

	$Re_2(CO)_{10}$		$Mn_2(CO)_{10}$	
Mode	Obsd.[c]	Calcd.	Obsd.[d]	Calcd.
ν_1	2125	2123	2111	2111
ν_2	1976	1976	1981	1981
ν_3	2070	2071	2044	2043
ν_4	1976	1976	1983	1983
ν_5	2014	2015	2013	2012
ν_6	2023	2026	2009	2010
ν_7	1976	1973	. . .	1953

[a] Frequencies in cm.$^{-1}$. [b] Method of calculation explained in text. [c] ν_3, ν_4, ν_5 from ref. 3; others from Raman spectrum reported here. [d] ν_3, ν_4, ν_5 from ref. 3; others deduced from overtone and combination bands reported here.

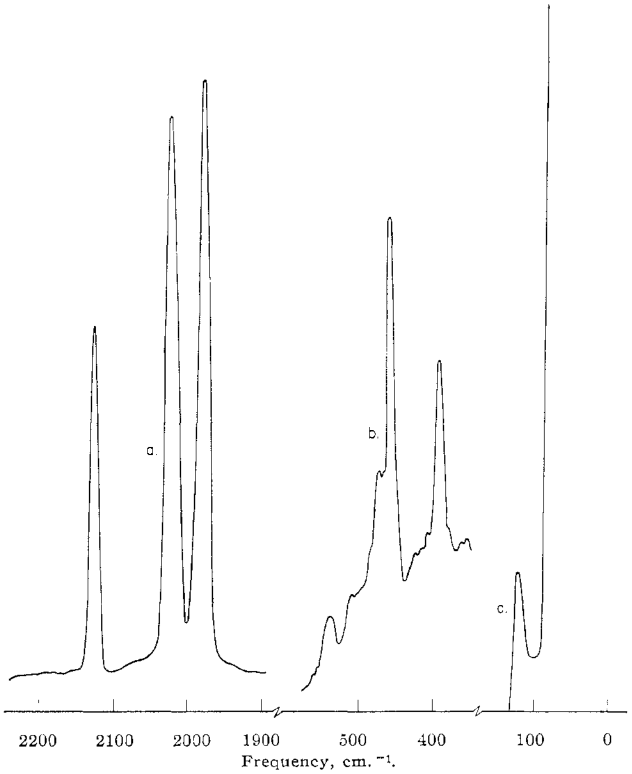

Figure 5.—Raman spectrum of solid $Re_2(CO)_{10}$: a, gain = 1000, slit = 10 cm.$^{-1}$; b, gain = 3000, slit = 5 cm.$^{-1}$; c, gain = 500, slit = 10 cm.$^{-1}$.

secular equations it follows that the Raman line of highest frequency must belong to ν_1, while it seems safe to assume (as explained in the previous section) that, despite the effects of coupling, the highest frequency infrared band will be ν_3, the one analogous to the highest frequency infrared band of $XMn(CO)_5$ molecules. Again, by analogy to the mononuclear species, the two remaining infrared bands are assigned to ν_5 and ν_4 in decreasing order of frequency. Also, we expect the Raman line of second highest frequency to belong to the mode derived from the B_1 modes of the $Re(CO)_5$ moieties, namely ν_6. This now leaves one observed Raman line (at 1976 cm.$^{-1}$) to be assigned and two expected Raman-active modes (ν_2 and ν_7) to be accounted for.

With the preceding assignments, we can use the secular equations to estimate the approximate frequency separation between ν_5 and ν_7, since the quantity $\nu_1^2 - \nu_3^2$ is approximately proportional to $4K$ while $\nu_5^2 - \nu_7^2$ is approximately proportional to $2\sqrt{2}K$. With the frequencies assigned to ν_1, ν_3, and ν_5, we estimate the frequency ν_7 to be 1974 cm.$^{-1}$. We therefore conclude that ν_2 and ν_7 are superposed or very nearly so. With this assignment, the force constants were computed using a computer program[11] which adjusts the constants to give the best least-squares fit of the calculated frequencies to the measured ones. The calculated frequencies are shown in Table III and the set of force constants is presented in Table IV.

TABLE IV

FORCE CONSTANTS (MDYNES/Å.) OF $M_2(CO)_{10}$ MOLECULES AND OF SOME $XM(CO)_5$ MOLECULES FOR COMPARISON

	Mn_2-$(CO)_{10}$	CH_3Mn-$(CO)_5$[a]	HMn-$(CO)_5$[b]	Re_2-$(CO)_{10}$	CH_3Re-$(CO)_5$[c]
k_1	16.06	16.13	16.42	15.92	15.97
k_2	16.33	16.87	16.93	16.57	16.87
k_i	0.23	0.25	0.26	0.26	0.30
K	0.33	. . .	. . .	0.24	. . .
k_j	−0.12	. . .	. . .	−0.04	. . .

[a] From ref. 9c. [b] From ref. 3. [c] From unpublished work of the authors.

In order to check the above assignments for $Re_2(CO)_{10}$ and in order to make a complete assignment of CO frequencies in $Mn_2(CO)_{10}$, for which Raman data are not available, we now consider the infrared-active combinations and overtones of the CO stretching modes of an $M_2(CO)_{10}$ molecule. Part A of Table V shows the relevant selection rules. Part B of the same table shows that we may expect to see six well-separated absorption bands in the infrared, and that the observed bands correspond quite well with those expected. Table V(B) also shows the observed combination and overtone bands for $Mn_2(CO)_{10}$, assigned by analogy with the $Re_2(CO)_{10}$ assignment. The near-infrared spectra are shown in Figure 4. The frequencies of the Raman-active bands of $Mn_2(CO)_{10}$ determined from these combinations and overtones are listed in Table III along with the frequencies observed for the infrared-active fundamentals of $Mn_2(CO)_{10}$. The set of force constants for $Mn_2(CO)_{10}$, computed in the same way as were those for $Re_2(CO)_{10}$, are given in Table IV and the calculated frequencies are listed in Table III.

Discussion

It has already been shown that the treatment developed in this paper satisfactorily accounts for the major qualitative differences between the infrared spectra of typical $XM(CO)_5$ and $M_2(CO)_{10}$ molecules. It is also evident that a self-consistent assignment of the infrared- and Raman-active CO stretching fundamentals as well as their infrared-active combinations and overtones can be made.

Nevertheless, it is important to emphasize that the model used is recognized to be crude and somewhat arbitrary in its details. Given the basic premise of a repulsive interaction between the electron density in

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(11) J. H. Schactschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

TABLE V

COMBINATIONS AND FIRST OVERTONES OF CO STRETCHING MODES FOR $M_2(CO)_{10}$ MOLECULES WITH D_{4d} SYMMETRY[a]

(A) Selection Rules

$(A_1)^2 = A_1$	R	$A_1B_2 = B_2$	IR	$B_2E_2 = E_2$	R
$(B_2)^2 = A_1$	R	$A_1E_1 = E_1$	IR	$B_2E_3 = E_1$	IR
$(E_1)^2 = A_1 + E_2$	R[b]	$A_1E_2 = E_2$	R	$E_1E_2 = E_1 + E_3$	R, IR
$(E_2)^2 = A_1 + B_1 + B_2$	R, IR[b]	$A_1E_3 = E_3$	R	$E_1E_3 = B_1 + B_2 + E_2$	R, IR
$(E_3)^2 = A_1 + E_2$	R[b]	$B_2E_1 = E_3$	R	$E_2E_3 = E_1 + E_3$	R, IR

(B) Expected and Observed Bands

$Re_2(CO)_{10}$			Assignments		$Mn_2(CO)_{10}$
Expected	Found	$Re_2(CO)_{10}$	Common	$Mn_2(CO)_{10}$	Found
4195	4193		$\nu_1 + \nu_3$		4156
4139	4137		$\nu_1 + \nu_5$		4124
4101	4098		$\nu_1 + \nu_4$		4093
4046	4057 sh		$\nu_2 + \nu_8$		4034
	4052	$\nu_3 + \nu_7$	$2\nu_6$	. . .	
4037	4036		$\nu_5 + \nu_6$		4020
3999	4005 sh	$\nu_6 + \nu_7$			
	3997	$\nu_5 + \nu_7$			
3990	3981 sh		$\nu_2 + \nu_5$	$\nu_3 + \nu_7$	3992
3952	3948	$\nu_4 + \nu_7$	$\nu_2 + \nu_4$	$\nu_6 + \nu_7$	3959
				$\nu_5 + \nu_7$	
				$\nu_4 + \nu_7$	3941?

[a] R = Raman active; IR = infrared active. [b] For overtones only.

$d\pi$ orbitals of the different metal atoms, there are other ways in which this could have been introduced into the potential energy function, thus leading to algebraically different expressions and numerically different constants. The procedure actually used was selected solely for its simplicity. While we believe that the repulsive interaction we have emphasized represents the major factor in the problem, it is not, of course, the sole one. It would therefore be pretentious to give it other than the simplest algebraic embodiment.[12]

Another consideration which argues against any more elaborate implementation of the basic idea is the probable lack of precision in the frequencies used. This inexactness stems from: (1) use of frequencies measured in different condensed phases, and (2) neglect of anharmonicity. Uncertainties of as much as 10–15 cm.$^{-1}$ are easily possible because of these factors. The fact that the interaction constant k_j appears to be zero or negative should not necessarily be given a literal physical interpretation. The main way in which its influence on the frequencies can be observed is in the separation $\nu_2^2 - \nu_4^2$, which is approximately proportional to $2k_j$, and this separation is approximately zero. However, ν_2 was measured on a solid sample of $Re_2(CO)_{10}$ while ν_4 was measured using a cyclohexane solution. Since frequencies are usually lowered more, relative to the gas phase values, in solids than in nonpolar solvents, a finite difference between ν_2 and ν_4 presumably exists. A difference of 20 cm.$^{-1}$ would lead to a value of 0.1 for k_j.

Another way k_j can be influenced is through the mixing of the pure axial CO stretches with the pure radial CO stretches (the A_1 and B_1 factored blocks of the secular determinant), which occurs to the same extent as in the methylpentacarbonylmanganese compound. Indeed the fact that the mixing (probably the primary mechanism for the intensity gain of the ν_1 vibration for $XMn(CO)_5$ compounds) is the same lends credibility to the physical model used here in respect to the relatively large intensity of ν_3.

The comparison of the force constants k_1, k_2, and k_t for the $M_2(CO)_{10}$ molecules with the corresponding constants for some $XM(CO)_{10}$ molecules in which the group X is of relatively low electronegativity and small or negligible π-accepting ability, as given in Table IV, shows that there is some difference in the electronic structure of an $M(CO)_5$ moiety in the two sorts of compounds. This is most obvious in the shift of ν_3 monomer to ν_6 dimer, some 20 cm.$^{-1}$ downward (see Figure 3). However, the main differences in spectra are due to the coupling between the two $M(CO)_5$ moieties in the dinuclear species. Thus, once again, we find that inferences regarding the electronic structures of metal carbonyl molecules made directly from the vibrational frequencies are unsafe. It is necessary to use some sort of simple treatment of the vibrational modes, such as the kind developed in this series of papers, in order to make at least a rough allowance for the effects of coupling between the individual internal deformation coordinates.

Finally, we tentatively report the first observed metal–metal stretching frequency for a polynuclear metal carbonyl. A Raman line at 120 cm.$^{-1}$ in $Re_2(CO)_{10}$ seems most likely to have such an assignment, although the possibility of its being due to a normal mode involving mainly C–Re–C bending cannot be completely ruled out. The force constant for the Re–Re bond, estimated from this frequency, is about 0.8 mdyne/Å. This constant may be compared with those[13] for Cd_2^{2+} (1.1 mdynes/Å.) and Hg_2^{2+} (around

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(12) This is an application of Ballhausen's rule: "Simple problems ought to be solved by simple means, and the heavy artillery spared until it is needed": C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, p. 25.

(13) J. D. Corbett, *Inorg. Chem.*, **1**, 700 (1962).

2.5 mdynes/Å., but variable since the Hg–Hg distance is a function of the anions in the compound), and also with that for the I_2 molecule (1.7 mdynes/Å.), which has a bond energy of 36 kcal./mole.

Experimental

The rhenium carbonyl was a gift of Alpha Inorganics. The powder sample was compressed into a wafer and the Raman spectrum was recorded using a Cary Model 81 Raman spectrophotometer. We are grateful to Professor R. C. Lord and Dr. Claron Hoskins for their assistance with these measurements. Due to the small quantity of material available and the difficulties inherent in the measurement of Raman spectra of solid materials, accurate measurements of the polarizations of the bands were not possible. For all bands the polarization ratios were found to be 0.65 ± 0.15. These results are not inconsistent with the assignments made, but they do not provide any definite support for them either.

The overtone and combination spectra were recorded on a Cary Model 14 spectrograph, using solutions in fresh Fisher Certified reagent carbon tetrachloride in quartz cells of path length 5 cm. Monitoring of the $Mn_2(CO)_{10}$ solution with infrared in the 2200–1900 cm.$^{-1}$ region immediately indicated slight reaction to form $ClMn(CO)_5$ (*i.e.*, the strongest $\nu_4(E)$ band of $ClMn(CO)_5$ was barely perceptible). The $ClMn(CO)_5$ combination band $\nu_2 + \nu_4$ appeared at 4200 cm.$^{-1}$ in the near-infrared spectrum at fairly low intensity, about 10% of the strongest $(\nu_1 + \nu_5)$ band of $Mn_2(CO)_{10}$ (see Figure 4). A near-infrared spectrum of $ClMn(CO)_5$ was run and indicated that the band at 4200 cm.$^{-1}$ is stronger by a factor of about 2 than the two next strongest bands. When dilute solutions of $Mn_2(CO)_{10}$ are prepared using previously opened, shelf aged CCl_4, the major constituent is $ClMn(CO)_5$.

Contribution from Mellon Institute, Pittsburgh, Pennsylvania, and
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Metal Nitrosyls. VI. Some New Six-Coordinate Mononitrosyl Complexes of Cobalt[1]

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A new series of six-coordinated mononitrosyl complexes of cobalt has been prepared. These complexes, stabilized using the bidentate ligands ethylenediamine and *o*-phenylenebis(dimethylarsine), are of the type $[CoXNOL_2]^+$. The infrared and electronic spectra of these mononitrosyl complexes show them to be complexes of cobalt(III). One five-coordinate cobalt compound has also been prepared and is discussed.

Introduction

Numerous cobalt nitrosyls have been prepared before,[3] but there are only two nitrosyl compounds in which cobalt is known to be six-coordinated. These two compounds contain the $[Co(CN)_5NO]^{3-}$ and the black $[CoNO(NH_3)_5]^{2+}$ ions.[4,5] In order to interpret the spectroscopic behavior of metal nitrosyls more easily, it was desirable to prepare a series of six-coordinated complexes which were relatively stable, which contained only a single nitrosyl group as one of the six ligands, and which could be readily compared with compounds of a similar geometry.

The ligands ethylenediamine (en) and *o*-phenylenebis(dimethylarsine) (das), first prepared by Chatt and Mann,[6] were selected as the stabilizing ligands since so many compounds of cobalt containing these ligands are known. The compounds $[CoX_2(das)_2]$ can be isolated as stable crystalline solids.[7] Therefore, these compounds were selected initially for reaction with NO.

Experimental

Materials and Analyses.—All of the reactions were carried out under nitrogen which was passed over pellets of "BTS" catalyst obtained from Badische-Anilin and Soda Fabrik, Ludwigshafen, Germany. This treatment is supposed to reduce the oxygen level in the nitrogen to 0.1 p.p.m. The compounds $[CoX_2(das)_2]$ were prepared as has been previously described.[7] The en complexes of cobalt(II) were prepared *in situ* and allowed to react with NO without isolation. The nitric oxide supplied by Matheson was purified by passing it through a trap at −78° and leading the effluent directly into the reaction vessel. No precautions were taken to remove water from the solvents, since it appeared that the reactions were not influenced by the presence or absence of water in the reaction media. The cobalt salts were obtained from City Chemical Corp. and Fisher Scientific Co.

The elemental analyses were carried out by Huffman Microanalytical Laboratories, Wheatridge, Colo.; Messrs. Weiler and Strauss, Oxford; Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.; and the University College Analytical Laboratory.

Reactions of NO with $[CoX_2(das)_2]$.—A sample of the cobalt(II) complex $[CoX_2(das)_2]$ was suspended or dissolved in the appropriate solvent, the system was purged with oxygen-free nitrogen, and NO_2-free NO was bubbled through the solution. When the reaction was complete, as indicated by the color or solubility of the materials, the undissolved solids were removed from the solu-

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[1] Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 30–Sept. 4, 1964. For the previous paper in this series, see R. D. Feltham and W. G. Fateley, *Spectrochim. Acta*, **20**, 1081 (1964).

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[3] For example, see (a) A. Earnshaw, P. C. Hewlett, and L. F. Larkworthy, *Nature*, **199**, 483 (1963); (b) W. Hieber and K. Heinicke, *Z. anorg. allgem. Chem.*, **316**, 305 (1962); (c) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

[4] (a) R. D. Feltham, *Inorg. Chem.*, **3**, 1038 (1964); (b) E. P. Bertin, S. Mizushima, T. J. Lance, and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 382 (1959).

[5] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 38 (1958).

[6] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 610 (1939).

[7] R. S. Nyholm, *ibid.*, 2071 (1950).